THE PREPARATION, PROPERTIES,
CHEMICAL BEHAVIOR, AND IDENTIFICATION OF

ORGANIC CHLORINE COMPOUNDS

By Ernest Hamlin Huntress

A Brief Introduction to the Use of Beilstein's
Handbuch der organischen Chemie

The Preparation, Properties, Chemical Behavior, and
Identification of Organic Chlorine Compounds
Tables of Data on Selected Compounds of Order III

By Ernest Hamlin Huntress and the late Samuel Parsons Mulliken

Identification of Pure Organic Compounds
Tables of Data on Selected Compounds of Order I
(Compounds of Carbon with Hydrogen or with Hydrogen and Oxygen)

THE PREPARATION, PROPERTIES,

CHEMICAL BEHAVIOR, AND IDENTIFICATION OF

ORGANIC CHLORINE COMPOUNDS

Tables of Data on
Selected Compounds of Order III

By
ERNEST HAMLIN HUNTRESS
Professor of Organic Chemistry
Massachusetts Institute of Technology

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PREFACE

This volume represents the second to appear in the series of Tables of Data prepared by the present author. It presents in organized and conveniently usable form a summary of data on a selected list of organic compounds containing carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen, and chlorine, or carbon, hydrogen, oxygen, and chlorine. Such compounds may more briefly be described as comprising Order 3.

Although users of its predecessor will immediately recognize many aspects of similarity in this book, they will also note in this volume certain differences. These distinctions are more fully discussed in Chapter I, but certain general aspects may be noted here.

Whereas the treatment of Order 1 compounds was directed mainly toward the aspect of identification, and though this point of view is vigorously continued, the present treatment of compounds of Order 3 has been expanded to include also the preparation, properties, and general chemical behavior of the individuals selected for treatment.

A second major difference from the earlier volume is in the extent of reference to the original literature or the corresponding abstracts thereof. This documentation is carried to a degree which may suggest to organic chemists that this volume comprises a Beilstein. The author hastens to disclaim any such degree of completeness for this work but does admit that for each compound selected a meticulous search of the literature through 1945 has furnished the basis for appropriate selection and systematic grouping of the aspects to be treated.

A third important difference from the earlier volume is the inclusion of references to patents as well as scientific articles. Though such patent references are treated with reserve, it is believed that they will be of interest to all users and of special value to industrial chemists. Throughout the book emphasis is given to industrial aspects since the rapid growth of this field during the last two decades, particularly in the United States, has resulted in the production and large-scale utilization of many individual compounds of this order (3).

A fourth type of difference in the present treatment as compared with that of Order 1 is seen in the tabulation of physical constants. In the earlier volume an attempt was made to select the "best" values. This process tended to conceal the magnitude and nature of the available constants from

CONTENTS

ABBREVIATIONS

	A
$[\alpha]_D^{20}$	specific rotation at 20° for D line
Ā	represents acid residue in whose description it occurs
abs.	absolute; absolutely
abt.	about
abund.	abundant
abv.	above
Ac	acetyl radical, i.e., $CH_3.CO$—
AcOEt	ethyl acetate
AcOH	acetic acid (glacial acetic acid when unmodified)
Ac_2O	acetic anhydride
ac.	acid
acc.	according
acid.	acidify, acidified, acidification
act.	active
addn.(l)	addition (additional)
adj.	adjacent (e.g., 1,2,3)
alc.	alcohol (95% unless otherwise stated); alcoholic
ald.	aldehyde
alk.(y)	alkali; alkaline; (alkalinity)
alm.	almost
Am	amyl
ammon.	ammoniacal
amorph.	amorphous
amt.(s)	amount(s)
anal.	analysis; analyses
anhyd.	anhydrous
anti-	anti (stereomeric opposite of *syn-*)
apprec.	appreciable; appreciably
approx.	approximate; approximately
aq.	water or aqueous
arom.	aromatic
assoc.(d) (n)	associate(s) (associated) (association)
	B
B̄	represents a molecule of the "basic" salt-forming compound in whose *description* it occurs
B.B.No.	bromide-bromate number
bibl.	bibliography
bkn.	"broken" (cf. color terminology)
boilg.	boiling
b.p.	boiling point (at atm. pressure unless specified)
Bu	*n*-butyl
bril.	brilliant
brn.	brown
Bz	benzoyl, i.e., $C_6H_5.CO$—
BzOH	benzoic acid
	C
C	Centigrade degrees
C̄	used to designate the compound in whose description it occurs
calc.(d) (n)	calculate(d) (calculation)
cap.	capillary
cat.	catalyst; catalytic; catalyzed
cc.	cubic centimeter(s)
cf.	compare
cg.	centigram(s)
charac.	characteristic
chem.	chemical
cis-	stereochemical opposite of *trans-*
cm.	centimeter(s)

coeff.	coefficient
col.(n)	*color (coloration)*
comb.(d) (n) (g)	combine(d) (combination) (combining)
comml.	commercial
compd.	*compound*
compn.	composition
conc.(d) (n)	concentrate(d) (concentration)
condens.	condensation
cond.	condition(s)
confrm.(n)	confirm; confirmatory (confirmation)
const.	constant
cont.(s) (g)	contain(s) (containing)
conv.(n)	convert (conversion)
cor.	corrected
corresp.	corresponding
C.P.	chemically pure
cpd.	compound
crit.	critical
cryst.(n) (d)	crystal(s); crystallize(s) *(d); crystalline* (crystallization)
C.S.T.	critical solubility temperature

D

Ⓓ	derivative (used to introduce important derivatives for specific characterizations)
(D)	dark (following name of a broken color)
D_4^{20}	density at 20° referred to water at 4°
d-	dextrorotatory
dec.(d) (n)	decompose(s) (decomposed) (decomposition)
deliq.	deliquesce(s), deliquescent
depolym.(d) (n)	depolymerize(s) (depolymerized) (depolymerization)
deriv.(s) (d) (n)	derivative(s) (derived) (derivation)
desic.	desiccator; desiccated
detectn.	detection
detn.(d)	determine; determination (determined)
diam.	diameter
dif.	*different; difference; difficultly*
dil.(td) (tg) (n)	dilute (diluted) (diluting) (dilution)
dimin.	*diminish; diminishing; diminished; diminutive*
dis.(lvd)	dissolve (dissolved)
dissoc.(d) (g) (n)	dissociate(d) (dissociating) (dissociation)
dist.(d) (g) (n)	distil(led) *(distilling)* (distillation)
distrib.(n)	distribute *(distribution)*
div.(n)	divide (division)
dk.	dark
d,l-	racemic (by external compensation as contrasted with *meso*)
D.V.	Duclaux Value

E

eas.	easily
efferv.	effervesce(s); effervescent
equiv.	equivalent
espec.	especially
est.(d) (g) (n)	estimate(s) (estimated) (estimating) (estimation)
Et	ethyl, i.e., $CH_3.CH_2$—
EtOH	ethyl alcohol (generally refers to 95% if unmodified)
eth.	ether (generally means ordinary diethyl ether)
evap.(d) (g) (n)	evaporate(d) (evaporating) (evaporation)
evol.(n)	evolve(s) (evolution)
exam.(d) (n)	examine(d) (examination)
expt.(l)	experiment(al)
ext.(d) (g) (n)	extract(s) (extracted) *(extracting) (extraction)*

F

filt.(n)	filter(s); filtrate (filtration)
floc.	flocculate; flocculent
fluores.	fluoresce(s); fluorescent

f.p.	freezing point
freq.	frequently
fract.(n) (nl)	fraction; fractionate (fractionation) (fractional)
fum.	fumaroid (stereochemical opposite of *maleinoid*)
fumg.	fuming
fus.(n)	fuse(s), melt(s); fusible; fusing (fusion)

G

g.	gram(s)
gem.	geminate (said of two like groups attached to same atom)
geom.	geometrical
glac.	glacial
gr.	green
grad.	graduate; graduated; gradually
gran.	granular; granulated

H

H.E.	hydrolysis equivalent
hexag.	hexagon, hexagonal
hr.(s)	hour(s)
ht.(d) (g)	heat(ed) (heating)
hydrol.(g) (zd)	hydrolyze; hydrolysis; (hydrolyzing) (hydrolyzed)
hygros.	hygroscopic

I

ibid.	in the same place
ident.	identical; identity
identif.(d) (n)	identify (identified) (identification)
i.e.	that is
immed.	immediate; immediately
impt.	important
inact.	inactive; inactivated
indef.	indefinite
indic.	indicate; indicator; indicated
inf.	infinite
inorg.	inorganic
insol.(y)	insoluble (insolubility)
irreg.	irregular
irrit.(n)	irritating (irritation)
isom.(d) (n)	isomer; isomerize (isomerized) (isomerization)

K

k	ionization constant

L

(L)	Light (modifying name of a broken color)
l-	laevorotatory
l.	liter(s)
lft(s).	leaflet(s)
lgr.	ligroin
liq.	liquid; liquefy
lt.	light (of a color)

M

(M)	medium (modifying name of a broken color)
m.	melt(s)
m-	meta
mal.	maleinoid (stereochemical opposite of *fumaroid*)
max.	maximum
Me	methyl, i.e., CH_3—
MeOH	methanol, i.e., CH_3OH
m.e.	milliequivalent
mg.	milligram(s)
mic.	micro
microcryst.	microcrystalline
min.	minute(s); minimum
minl.	mineral
misc.	miscellaneous; miscible
mixt.	mixture(s)
mod.	moderate
modifn.	modification
mol.	molecular
monoclin.	monoclinic
ml.	milliliter
mm.	millimeter
m p.	melting point
ms	meso-

N

N	normal (equivalents per liter)
n	normal
n_D^{20}	refractive index at 20° for D line of sodium
ndl.(s)	needle(s)
neg.	negative
Neut. Eq.	neutralization equivalent
neut.(zd)	neutral (neutralized)
no.	number
non-fus.	non-fusible
non-vol.	non-volatile

O

o-	ortho
obs.(d) (n)	observe(d) (observation)
obt.(d)	obtain(ed)
opt.	optical
optim.	optimum
or.	orange
ord.	ordinary
orig.	original; originally
org.	organic
oxid.(g) (n)	oxidize(s) (oxidizing) (oxidation)

P

Ⓟ	preliminary test
p-	para
perm.	permanent
pet.	petroleum
Ph	phenyl, i.e., C_6H_5—
phys.	physical
physiol.	physiological
Pk	picryl, i.e., 2,4,6-trinitrophenyl-
PkOH	picric acid
pl.	plate(s)
polym.(n)	polymer; polymerize; polymerized (polymerization)
pos.	positive
powd.	powder; powdered
ppt.(d) (g) (n)	precipitate(d) (precipitating) (precipitation)
Pr	propyl
pr.	prism(s)
pract.	practically
prep.(d) (g) (n)	prepare(d) (preparing) (preparation)
pres.	presence
press.	pressure
prim.	primary
prin.	principal
prismat.	prismatic
prob.	probably
proc.	procedure
prod.	product; produce; produced
prop.	property; properties
pt.(s)	part(s)
pulv.(d)	pulverize(d)
pung.	pungent
purif.(d) (g) (n)	purify (purified) (purifying) (purification)

Q

quad.	quadratic
qual.	qualitative; qualitatively
quant.	quantity; quantitative; quantitatively
quat.	quaternary
q.v.	quod vide (which see)

R

rac.	racemic
rap.	rapid; rapidly
reactn.	reaction(s)
reagt.(s)	reagent(s)
rearr.	rearrange(s); rearrangement
recommd.	recommend; recommended
recryst.(d) (g) (n)	recrystallize(d) (recrystallizing) (recrystallization)
rect.	rectangular
redis.	redissolve
reduc.(d) (g) (n)	reduce(d) (reducing) (reduction)
ref.	reference
reminis.	reminiscent
reppt.(d) (g) (tn)	reprecipitate(d) (reprecipitating) (reprecipitation)

resid.	residue; residual
resin.	resinify; resinification
resp.	respectively
rhomb.	rhombic

S

Sap. Eq.	saponification equivalent
sapon.(d) (g) (n)	saponify (saponified) (saponifying) (saponification)
sat.(d) (g) (n)	saturate(d) (saturating) (saturation)
sec.	second(s)
sec.	secondary
sect.	section
sep.(d) (g) (n)	separate(d) (separating) (separation)
sft.(n)(s)	soft; soften(s)
shak.(g) (n)	shake (shaking) (shaken)
sint.(d)	sinter(s) (sintered)
sl.	slightly
sld. cap.	sealed capillary
S.N.	system number (Beilstein)
spar.	sparing; sparingly
sol.(n) (y)	soluble (solution) (solubility)
solv.	solvent(s)
sp gr.	specific gravity
sq.	square
subl.(g)	sublimes; sublimate; subliming; sublimation
subl. w.m.	sublimes without melting
subseq.	subsequent
subst.	substance; substantially; substituted
suff.	suffices; sufficient
supersat.(d)(g)(n)	supersaturate(d)(supersaturating) (supersaturation)
st.	steam
s t.	sealed tube
stdg.	standing
sym.	symmetrical
syn-	stereochemical opposite of *anti-*
syst.	system; systematic; systematically

T

T	Numbered Test
tbl.(s)	tablet(s); tabular
tech.	technical
temp.	temperature
theor.	theoretical
therm.	thermometer
T.N.B.	1,3,5-trinitrobenzene
T.N.T.	2,4,6-trinitrotoluene
ter-	tertiary
trans-	stereochemical opposite of *cis-*
transf.	transfer; transform
tt.	test tube

U

u.c.	uncorrected
undec.	undecomposed
undislvd.	undissolved
unoxid.	unoxidized
unsat.	unsaturated
unsym.	unsymmetrical
U.S.P.	United States Pharmacopœia
u.v.	ultra violet

V

vac.	vacuum
vap.	vapor; vaporize
var.	variable
vic.	vicinal (adjacent)
vig.	vigorous; vigorously
viol.	violent; violently; violet
visc.	viscous
volat.(g) (n)	volatile (volatilizing) (volatilization)
volumin.	voluminous

W

warm.	warming
wh.	white
wt.	weight

Y

yel.	yellow

MEMORANDUM OF CERTAIN 1946–1947 REFERENCES NOT INCORPORATED IN REGULAR TEXT

The regular text of this book is made up of references selected from the chemical literature through the year 1945. Owing to the disturbed postwar conditions of the publishing and printing trades, and also to the exceptional difficulty and magnitude of this work, almost three years have elapsed since the termination of the period of writing of the organized text. Inevitably, there have appeared during this period many scientific papers whose content would gladly have been incorporated appropriately in the regular text. For practical reasons, however, such continuous adjustment was obviously impossible.

In an effort to avoid so far as possible complete loss of such material, however, certain of the more important papers which have come to the attention of the author during the 1946–1947 period have been listed in the following supplementary bibliography. Articles relevant to more than a single numbered compound are cited under the first in such a numerical series, cross-references being given under subsequent compounds to avoid excess duplication of references. In the interests of brevity, clarity, and consistency of nomenclature, slight modifications of the actual titles of the original papers have sometimes been made for purposes of this listing.

General

(1) Table of azeotropes and nonazeotropes
Horsley, *Ind. Eng. Chem., Anal. Ed.* **19**, 508–600 (1947)
[illegible] its accompanying formula index and [illegible] valuable and includes so many of the [illegible] that it is placed at the head of this supplementary reference list without further cross-reference to it from subsequent entries below.

3:0075 **δ-Chloro-*n*-valeric acid**

(2) Isomeric chlorinated long-chain esters
Guest, *J. Am. Chem. Soc.* **69**, 300–302 (1947)
—**Methyl δ-chloro-*n*-valerate:** b.p. 89–92° at 18 mm. [From δ-chloro-*n*-valeronitrile 80% H_2SO_4 refluxed 50 hr.]

3:0235 **α-Chloroisobutyric acid**

(3) The chloro- and bromoisobutyronitriles
Stevens, *J. Am. Chem. Soc.* **70**, 166 (1948)
Ⓓ **α-Chloroisobutyramide:** cryst. from EtOAc, m.p. 115–118°; from aq., m.p. 117–119°. [From α-chloroisobutyryl chloride (3:5385) with conc. NH_4OH at 10° in 70% yield]

3:0280 **Chloromaleic anhydride**

(4) Use of Ĉ in determination of conjugated diolefins
Putnam, Moss, Hall, *Ind. Eng. Chem., Anal. Ed.* **18**, 628–630 (1946)

3:0460 *β*-**Chloropropionic acid**
(5) Convenient synthesis of *β*-chloropropionitrile (from acrylonitrile with hydrogen chloride)
Stewart, Clark, *J. Am. Chem. Soc.* **69**, 713–714 (1947)

3:0885 *α*-**Chloro-diphenylacetyl chloride**
(6) $\overline{C}$ as reagent for preparation of benzilic acid esters of tertiary amino alcohols
King, Holmes, *J. Chem. Soc.* **1947**, 164–168; *C.A.* **41**, 5121 (1947)

3:1150 Trichloroacetic acid
(7) Kinetics of the decomposition of certain salts of $\overline{C}$ in ethanol-water mixtures
Hall, Verhoek, *J. Am. Chem. Soc.* **69**, 613–616 (1947)
(8) Kinetics of the decomposition of $\overline{C}$ in formamide-water mixtures
Cochran, Verhoek, *J. Am. Chem. Soc.* **69**, 2987–2988 (1947)

3:1212 Phenacyl chloride
(9) The reaction of $\overline{C}$ with phenylhydrazine
van Alphen, *Rec. trav. chim.* **65**, 112–116 (1946); *C.A.* **41**, 409 (1947)

3:1370 Chloroacetic acid
(10) New method for the detection and determination of $\overline{C}$ (using pyridine)
Ramsey, Patterson, *J. Assoc. Offic. Agr. Chemists* **29**, 100–111 (1946); *C.A.* **40**, 3369 (1946)
(11) Effect of *p*H on rate of hydrolysis of $\overline{C}$
Berhenke, Britton, *Ind. Eng. Chem.* **38**, 544–546 (1946)

3:1420 1,1,1-Trichloro-2,2-diphenylethane
(12) Derivatives of $\overline{C}$
[illegible] –2268 (1947)
(13) [illegible] 343; *C.A.* **40**, 5040 (1946)

3:3298 1,1,1-Trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT")
(14) Methods of preparation of $\overline{C}$
Bailes, *J. Chem. Education* **22**, 122 (1945); *C.A.* **41**, 3085 (1947)
(15) Preparation of technical $\overline{C}$
Mosher, Cannon, Conroy, Van Strien, Spalding, *Ind. Eng. Chem.* **38**, 916–923 (1946)
(16) Preparation of $\overline{C}$ using HF as condensing agent
Simons, Bacon, Bradley, Cassaday, Heegberg, Tarrant, *J. Am. Chem. Soc.* **68**, 1613–1615 (1946)
(17) [illegible] (1946); *C.A.* **41**, 2409 (1947)
(18) [illegible] *ng. Chem.* **39**, 868–870, 1683 (1947)
(19) [illegible]
(20) [illegible] 5); *C.A.* **39**, 4695 (1945)
(21) [illegible] to the determination of $\overline{C}$ in water [illegible] 45); *C.A.* **40**, 2561 (1946)
(22) Field test for surface $\overline{C}$
Stiff, Castillo, *Ind. Eng. Chem., Anal. Ed.* **18**, 316–317 (1946)
(23) [illegible] **40**, 4842 (1946)
(24) [illegible] 6)
(25) Determination of *p,p′*-isomer in technical $\overline{C}$
Cristol, Hayes, Haller, *Ind. Eng. Chem., Anal. Ed.* **18**, 339 (1946)
(26) Determination of *p,p′*-isomer in technical $\overline{C}$
[illegible] *Anal. Ed.* **18**, 339 (1946)
(27) [illegible] a microscopical method
[illegible] *Anal. Ed.* **18**, 578–582 (1946)
(28) [illegible]
La Clair, *Ind. Eng. Chem., Anal. Ed.* **18**, 763–766 (1946)

(29) Determination of $\bar{C}$ as spray residue on fresh fruit by three independent methods
Wichmann, Patterson, Clifford, Klein, Claborn, *J. Assoc. Offic. Agr. Chemists* **29**, 188–190 (1946), *C.A.* **40**, 6705 (1946)
Method 1. Organic chlorine determinations
Klein, Wichmann, *ibid.* **29**, 191–195 (1946); *C.A.* **40**, 6705 (1946)
Method 2. The Shechter-Haller colorimetric procedure
Clifford, *ibid.* **29**, 195–206 (1946); *C.A.* **40**, 6705 (1946)
Method 3. 2,4-Dinitrophenylhydrazine method
Claborn, Patterson, *ibid.* **29**, 206–218 (1946), *C.A.* **40**, 6705 (1946)

(30) Decomposition and volatility of $\bar{C}$ and some of its derivatives
Wichmann, Patterson, Clifford, Klein, Claborn, *J. Assoc. Offic. Agr. Chemists* **29**, 218–222 (1946); *C.A.* **40**, 6740 (1946)

(31) –53 (1947)

(32)

(33) Determination of $\bar{C}$ by Shechter procedure, particularly in milk and fats
Clifford, *J. Assoc. Offic. Agr. Chemists* **30**, 337–349 (1947); *C.A.* **41**, 6839 (1947)

(34) Nature of the by-products in technical $\bar{C}$
Gätzi, Stammbach, *Helv. Chim. Acta* **29**, 563–572 (1946), *Experientia* **1**, 276 (1945), *C.A.* **40**, 5040–5041 (1946)

(35) Simple purification procedure for $\bar{C}$
K. H. Cook, W. A. Cook, *J. Am. Chem. Soc.* **68**, 1663–1664 (1946)

(36) Applications of infrared spectroscopy to $\bar{C}$
Downing, Freed, Walker, Patterson, *Ind. Eng. Chem., Anal. Ed.* **18**, 461–467 (1946)

(37) Some derivatives of $\bar{C}$
Backeberg, Marais, *J. Chem. Soc.* **1945**, 803–805; *C.A.* **40**, 1156, 5717 (1946)

(38) Bromine analogs of $\bar{C}$
Cristol, Haller, *J. Am. Chem. Soc.* **68**, 140–141 (1946)

(39) Crystal structure of $\bar{C}$ and relatives
Wild, Brandenberger, *Helv. Chim. Acta* **29**, 1024–1040 (1946), *C.A.* **41**, 428 (1947)

(40) Synthesis of some analogs of $\bar{C}$
Kirkwood, Dacey, *Can. J. Research* **24-B**, 69–72 (1946); *C.A.* **40**, 5717 (1946)

(41) Catalytic decomposition of $\bar{C}$
Fleaner, *J. Am. Chem. Soc* **68**, 2399 (1946)

(42) Inhibition of catalyzed thermal decomposition of $\bar{C}$
Gunther, Tow, *J. Soc. Chem. Ind.* **66**, 57–59 (1947), *C.A.* **41**, 5675 (1947)

(43) Dehydrohalogenation of $\bar{C}$
Wain, Martin, *Nature* **159**, 68–69 (1947); *C.A.* **41**, 2715 (1947)

(44) Estimation of $\bar{C}$ by methods depending upon dehydrohalogenation
Wain, Martin, *Analyst* **72**, 1–6 (1947); *C.A.* **41**, 2198 (1947)

(45) Preparation of di-(p-chlorophenyl)acetic acid from $\bar{C}$
Grummitt, Buck, Egan, *Org. Syntheses* **26**, 21–23 (1946)

(46) Reactions of $\bar{C}$ and associated compounds
Forrest, Stephenson, Waters, *J. Chem. Soc.* **1946**, 333–339; *C.A.* **40**, 5039–5040 (1946)

(47) Crystallization of $\bar{C}$ from binary melts
Gilpin, McCrone, Smedal, Grant, *J. Am. Chem. Soc.* **70**, 208–211 (1947)

3:3320 1,1-Dichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDD")

(48) Anhydrous $FeCl_3$ as rearrangement catalyst for some chlorinated diphenylethanes
Fleck, *J. Org. Chem.* **12**, 708–712 (1947)

3:3350 4,6-Dichlororesorcinol

(49) For preparation of isomeric 2,4-dichlororesorcinol see
Postovsky, Kuchina, *J. Gen. Chem. (U.S.S.R.)* **17**, 276–282 (1947); *C.A.* **42**, 534–535 (1948)

3:3331 *p*-Phenylphenacyl chloride

(50) Conversion of $\bar{C}$ to p-phenylphenacyl iodide
Rheinboldt, Perrier, *J. Am. Chem. Soc.* **69**, 3148–3149 (1947)

3:4093 2,4-Dichlorophenoxyacetic acid

(51) Preparation of $\bar{C}$ from phenol and chloroacetic acid
Ebel, Bell, Fries, Kasey, Berkebile, *J. Chem. Education* **24**, 449 (1947)

(52)

(53)

(54)
Freed, *J. Am. Chem. Soc.* 68, 2112 (1946)

3:4375 *p*-Chlorophenoxyacetic acid
(—) See reference (53) under 3:4095 (above).

3:4410 *cis*-1,2,3,4,5,6-Hexachlorocyclohexane
(55) Preparation of the benzene hexachlorides
Gunther, *Chemistry & Industry* 1946, 399; *C.A.* 41, 1625 (1947)
(56)

(57)

(58) Alkaline degradation of benzene hexachlorides
Gunther, Blinn, *J. Am. Chem. Soc.* 69, 1215–1216 (1947)
(59) The gamma isomer of hexachlorocyclohexane
Slade, *Chemistry & Industry* 1945, 314–319; *C.A.* 40, 2257–2259 (1946)
(60) The epsilon isomer of hexachlorocyclohexane
Kauer, DuVall, Alquist, *Ind. Eng. Chem.* 39, 1334–1338 (1947)
(61) Determination of hexachlorocyclohexane is impregnated cloth
Goldenson, Sass, *Ind. Eng. Chem., Anal. Ed.* 19, 320–322 (1947)

3:4612 Di-(*p*-chlorophenyl)acetic acid
(—) *Preparation from "DDT"; see reference (45) under 3:3298 (above)*

3:4835 Hexachloroethane
(62) Preparation of C by chlorination of liquid 1,1,2,2-tetrachloroethane and pentachloroethane
Pearce, *Can. J. Research* 24-F, 369–379 (1946); *C.A.* 40, 7151 (1946)

3:4947 Tetrachlorophthalic anhydride
(63) Reactions and uses of C
Lawlor, *Ind. Eng. Chem.* 39, 1419–1423 (1947)
(64)
47)
(65)
Nordlander, Cass, *J. Am. Chem. Soc.* 69, 2679–2682 (1947)

3:4990 *trans*-1,2,3,4,5,6-Hexachlorocyclohexane
(—) See references (55)–(61), inclusive, under *cis*-isomer (3:4410) (above)

3:5000 Carbonyl chloride (Phosgene)
(66) Heat capacity, entropy, vapor pressure, and heats of fusion and vaporization of C
Giaque, Jones, *J. Am. Chem. Soc.* 70, 120–124 (1948)
(67) . . . with benzene
. 38, 624–626 (1946)
(68) . . . *ons for formation of tetrasubstituted* ureas
Lastovskii, *J. Applied Chem.* (*U.S.S.R.*) 19, 440–444 (1946); *C.A.* 41, 1214 (1947)
(69) Reaction of C with *o*-aminobenzoic acid (to give 72–75% yield isatoic anhydride)
Wagner, Fegley, *Org. Syntheses* 27, 45–47 (1947)

3:5028 *trans*-1,2-Dichloroethylene
(70)

(71)

3:5042 *cis*-1,2-Dichloroethylene
(—) See references (70) and (71) under *trans*-isomer (3:5028) (above)

3:5050 Chloroform
(72) . . . 69, 1100–1105 (1947)
(73) . . . *Chem. Soc.* 69, 3045–3047 (1947)

3:5100 Carbon tetrachloride
(—) See references (72) and (73) under chloroform (3:5050) (above)
(74) Analysis of the system benzene/ethanol/carbon tetrachloride (by refractive indices and densities)
Campbell, Miller, *Can. J. Research* **25-B**, No. 3, 228–242 (1947); *C.A.* **41**, 6839 (1947)

3:5110 1,2-Dichloropropene-1 (low-boiling stereoisomer)
(—) See reference (70) under 3:5028 (above)

3:5130 1,2-Dichloroethane
(75) Reaction of $\bar{C}$ with benzene
Korshak, Kolesnikov, Kharchevnikova, *Compt. rend. acad. sci. U.R.S.S.* **56**, 169–172 (1947), *C.A.* **42**, 545 (1948)

3:5150 1,2-Dichloropropene-1 (high-boiling stereoisomer)
(—) See reference (70) under 3:5028 (above)

3:5170 1,1,2-Trichloroethylene
(—) See reference (70) under 3:5028 (above)
(76) Dimerization of $\bar{C}$
Henne, Ruh, *J. Am. Chem. Soc.* **69**, 279–281 (1947)

3:5190 2,3-Dichloropropene-1
(—) See reference (70) under 3:5028 (above)

3:5210 Trichloroacetaldehyde
(77) [illegible]
[illegible] 07 (1946); *C.A.* **40**, 3368 (1946)
(78) [illegible]
Shaw, Bruce, *Ind. Eng. Chem., Anal Ed* **19**, 884–885 (1947)
(79) Hydrolysis of $\bar{C}$ in heavy hydrogen water
Lander, Wright, *Nature* **158**, 381 (1946); *C.A.* **41**, 1998 (1947)

3:5220 2,3-Dichlorobutadiene-1,3
(80) Preparation of $\bar{C}$ from tri-, tetra-, and pentachlorobutanes
Klebanskii, Belen'kaya, Chevychalova, *J. Applied Chem.* (*U.S.S.R.*) **19**, 200–206 (1946), *C.A.* **41**, 685 (1947)
(—) See reference (85) under 3:5350 (below)

3:5280 1,3-Dichloropropene-1
(81) The *cis*- and *trans*-isomers of $\bar{C}$
Andrews, Kepner, *J. Am. Chem. Soc.* **69**, 2230–2231 (1947)
(82) The catalytic hydrolysis and characterization of $\bar{C}$
Hatch, Roberts, *J. Am. Chem. Soc.* **68**, 1196–1198 (1946)
(—) See reference (70) under 3:5028 (above)

3:5330 1,1,2-Trichloroethane
(83) Ternary liquid and binary vapor equilibrium of the system: acetone/water/$\bar{C}$
Treybal, Weber, Daley, *Ind. Eng. Chem.* **38**, 817–821 (1946)

3:5350 3,4-Dichlorobutene-1
(84) [illegible]
[illegible] 948)
(85) [illegible]
[illegible] *U.S.S.R.*) **17**, 235–252 (1947), *C.A.* **42**, 514–516 (1948)

3:5358 3-Chloro-1,2-epoxypropane ("Epichlorohydrin")
(86) Condensation of $\bar{C}$ with phenols in presence of BF_3
E. Levas, H. LeFebvre, *Compt. rend.* **222**, 555–557 (1946); *C.A.* **40**, 3737 (1946)
H. LeFebvre, E. Levas, Mme. E. Levas, *Compt. rend.* **222**, 1439–1440 (1946); *C.A.* **40**, 5712 (1946)

3:5425 Chloroacetone
(87) Condensation of $\bar{C}$ with formaldehyde
Hurd, McPhee, Morey, *J. Am. Chem. Soc.* **70**, 329–331 (1948)

3:5430 α,α-Dichloroacetone
(—) See reference (87) under 3:5425 (above)

3:5550 1,3-Dichlorobutene-2
(88) Oxidation of $\bar{C}$ with aqueous HNO_3 or $Ca(NO_3)_2$
Isagulyants, Mkryan, *Bull. Armenian Branch Acad. Sci. U.S.S.R.*, **1944**, No. 5/6,

(89)
Sci. U.S.S.R., **1944**, No. 5/6,

(90) *Gaseous products of action of zinc dust on C*
Tatevosyan, Vardanyan, *Bull Armenian Branch Acad. Sci. U.S.S.R.*, **1941**, No. 8, 75–78; *C.A.* **40**, 3394 (1946)
(91) Reaction of $\bar{C}$ with aromatic hydrocarbons
Isagulyants, Muscheghian, *Compt. rend. acad. sci. U.R.S.S.* **56**, 165–168 (1947); *C.A.* **42**, 530 (1948)

3:5552 2-Chloroethanol-1 (ethylene chlorohydrin)
(92) Determination of $\bar{C}$ (by hydrolysis and determination of chloride ion)
Uhrig, *Ind. Eng. Chem., Anal. Ed.* **18**, 469 (1946)
(93) Preparation and properties of β-chloroethyl esters of boric, silicic, and phosphoric acids
Jones, Thomas, Pritchard, Bowden, *J. Chem. Soc.* **1946**, 824–827; *C.A.* **41**, 390–391 (1947)
(94) Analysis of water-soluble chlorohydrins
Trafelet, *Analytical Chemistry* **20**, 68–69 (1948)

3:5590 1,3-Dichloro-2-methylpropene-1
(95) Preparation of *cis* and *trans* isomers of $\bar{C}$
Hatch, Russ, Gordon, *J. Am. Chem. Soc.* **69**, 2614–2616 (1947)

3:5633 3-Chloro-2-(chloromethyl)propene-1
(—) See reference (95) under 3:5590 (above)

3:5725
(—)

(—)

3:5750 1,1,2,2-Tetrachloroethane (acetylene tetrachloride)
(96) ystems containing isobutyl alcohol and $\bar{C}$
40 (1946)
(97)
Goldenson, Thomas, *J. Ind. Hyg. Toxicol.* **29**, 14–22 (1947); *C.A.* **41**, 1578 (1947)
(—) Chlorination of $\bar{C}$ as source of hexachloroethane
See reference (62) under 3:4835 (above)

3:5880 Pentachloroethane
(—) Chlorination of $\bar{C}$ as source of hexachloroethane
See reference (62) under 3:4835 (above)

3:5885 1,2,3-Trichloro-2-methylpropane
(—) See reference (95) under 3:5590 (above)

3:5900 1,3-Dichlorobutanone-2
(98) Formation of $\bar{C}$ from ethyl methyl ketone by vapor-phase chlorination
Rabjohn, Rogier, *J. Org. Chem.* **11**, 781–787 (1946)

3:5910 α,α,β-Trichloro-*n*-butyraldehyde ("Butyrchloral")
(99) Reaction of $\bar{C}$ with Grignard reagents
Floutz, *J. Am. Chem. Soc.* **68**, 2490–2491 (1946)

3:5960
(100)
(1946)

3:5985 1,3-Dichloropropanol-2 ("α-dichlorohydrin")
(101) Activated $\bar{C}$; a new colorimetric reagent for vitamin A
Sobel, Werbin, *Ind. Eng. Chem., Anal. Ed.* **18**, 570–573 (1946)
(102) Determination of vitamin A with activated $\bar{C}$: a comparison with spectrophotometric and $SbCl_3$ methods
Sobel, Werbin, *Ind. Eng. Chem., Anal. Ed.* **19**, 107–112 (1947)

3:6207 **Ethyl α-chloroacetate**
(103) Behavior of $\bar{C}$ with arylhydrazines
van Alphen, *Rec. trav. chim.* **64**, 305–308 (1945); *C.A.* **41**, 407 (1947)

3:6550 **p-Chlorobenzoyl chloride**
(104) Conversion of $\bar{C}$ with pyridine to p-chlorobenzoic acid
Allen, Kibler, McLachlin, Wilson, *Org. Syntheses* **26**, 1–3 (1946)

3:6878 **1-Chloronaphthalene**
(105) 1-Halonaphthalenes in the Friedel-Crafts reaction
Jacobs, Winstein, Ralls, Robson, *J. Org. Chem.* **11**, 27–33 (1946)

3:7005 **Methyl chloride**
(106) Determination of $\bar{C}$ in air
Franklin, Gunn, Martin, *Ind. Eng. Chem., Anal. Ed.* **18**, 314–316 (1946)
(107) Preparation of $\bar{C}$ (free from dimethyl ether)
Pieck, Courtoy, *Bull. soc. chim. Belg.* **56**, 65–71 (1947); *C.A.* **41**, 6524 (1947)

3:7010 **Vinyl chloride**
(108) Condensation of alkyl halides with monohalo-olefins
Schmerling, *J. Am. Chem. Soc.* **68**, 1650–1654 (1946)

3:7015 **Ethyl chloride**
(—) See reference (70) under 3:5028 (above)

3:7020 **2-Chloropropene-1**
(—) See reference (108) under 3:7010 (above)

3:7025 **2-Chloropropane (isopropyl chloride)**
(—) See reference (70) under 3.5028 (above)
(—) See reference (108) under 3:7010 (above)

3:7035 **3-Chloropropene-1 (allyl chloride)**
(109) [illegible]
[illegible] *ans. Am. Inst.*
(110) Conversion of $\bar{C}$ with Mg to hexadiene-1,5 (biallyl) in 55–65% yield
Turk, Chanan, *Org. Syntheses* **27**, 7–9 (1947)
(111) Condensation of $\bar{C}$ with aromatic hydrocarbons or aryl halides to give 1-aryl-2-chloropropanes
Patrick, McBee, Hass, *J. Am. Chem. Soc.* **68**, 1009–1011 (1946)
(—) See reference (108) under 3:7010 (above)

3:7040 **1-Chloropropane (n-propyl chloride)**
(—) See reference (70) under 3:5028 (above)

3:7045 **2-Chloro-2-methylpropane (ter-butyl chloride)**
(—) See reference (70) under 3 5028 (above)
(—) See reference (108) under 3:7010 (above)
(112) The $AlCl_3$-catalyzed addition of $\bar{C}$ to propylene
Miller, *J. Am Chem Soc.* **69**, 1764–1768 (1947)
(113) The condensation of $\bar{C}$ with cyclohexene
Schmerling, *J. Am. Chem. Soc.* **69**, 1121–1125 (1947)
(114) Formation of $\bar{C}$ by addition of hydrogen chloride to isobutylene
Mayo, Katz, *J. Am. Chem. Soc.* **69**, 1339–1348 (1947)
(115) The hydrolysis of $\bar{C}$ in 95% water/5% acetone solution
Swain, Ross, *J. Am. Chem. Soc.* **68**, 658–661 (1946)

3:7065 **Acetyl chloride**
(116) Ketene dimers from acid halides
Sauer, *J. Am. Chem. Soc.* **69**, 2444–2448 (1947)

3:7080 **2-Chlorobutadiene-1,3 (Chloroprene)**
(—) See reference (85) under 3:5350 (above)
(117) Composition and structure of dimers of $\bar{C}$
Klebanskii, Denisova, *J. Gen. Chem. (U.S.S.R.)* **17**, 703–716 (1947); *C.A.* **42**, 1215 (1948)

3:7085 **Chloromethyl methyl ether**
(118) Reaction of $\bar{C}$ with terpenes
Allard, *Bull. soc. chim. France* **1947**, 731–735; *C.A.* **42**, 890 (1948)

3:7170 **Propionyl chloride**
(—) See reference (100) under 3:5960 (above)
(—) *See reference (116) under 3:7065 (above)*

3:7210 **1-Chlorobutadiene-1,3**
(119) *Synthesis and properties of* $\overline{C}$
Petrov, Sopov, *J. Gen. Chem. (U.S.S.R.)* **15**, 981–987 (1945); *C.A.* **40**, 6406 (1945)
(—) See reference (85) under 3:5350 (above)

3:7220 **2-Chloro-2-methylbutane** (*ter*-**amyl chloride**)
(—) See reference (108) under 3:7010 (above)

3:7370 ***n*-Butyryl chloride**
(—) See reference (116) under 3:7065 (above)

3:7465 **4-Chloro-2-methylbutene-2**
(120) Formation of $\overline{C}$ from isoprene by addition of HCl
Jones, Chorley, J. Chem. Soc. **1946**, *832–833; C.A.* **41**, *386* (1947)

3:7560 **Isovaleryl chloride**
(—) *See reference (116) under 3:7065 (above)*

3:7598 **3-Chlorobutanone-2**
(—) *See reference (98) under 3:5900 (above)*

3:7650 **1,3-Dichlorobutene-1**
(121) The dichlorobutene prepared from crotonaldehyde
Andrews, *J. Am. Chem. Soc.* **68**, 2584–2587 (1946)

3:7865 **1,1-Dichlorobutene-2**
(—) See reference (121) under 3:7650 (above)

3:7740 ***n*-Valeryl chloride**
(—) See reference (116) under 3:7065 (above)

3:7747 **1-Chloropropanol-2 (propylene chlorohydrin)**
(—) See reference (94) under 3:5552 (above)

3:7925 **1,3-Dichlorobutane**
(122) Preparation of $\overline{C}$ and its Friedel-Crafts reaction with benzene
Sisido, Nozaki, *J. Am. Chem. Soc.* **69**, 961–964 (1947)

3:8012 **1-Chlorobutanone-2**
(—) See reference (98) under 3:5900 (above)

3:8110 ***d,l*-1-Chlorobuten-3-ol-2**
(123) Some reactions of $\overline{C}$
Bissinger, Fredenburg, Kadesch, Kung, Langston, Stevens, Strain, *J. Am. Chem. Soc.* **69**, 2955–2961 (1947)

3:8168 ***n*-Caproyl chloride**
(—) See reference (116) under 3:7065 (above)

3:8520 ***n*-Heptanoyl chloride**
(124) Conversion of $\overline{C}$ to *n*-heptanoic anhydride with pyridine
Allen, Kibler, McLachlin, Wilson, *Org. Syntheses* **26**, 1–3 (1946)

3:8535 [illegible]
(125) [illegible] eissgerber, Wilkins, Whitmore, *Ind. Eng.* [illegible]
(126) [illegible] *n preparation of benzylamines*
[illegible]
(127) [illegible] yl magnesium chloride and diethyl sulfate
[illegible])-2060 (1947)

3:8680 ***n*-Octanoyl chloride**
(—) See reference (116) under 3:7065 (above)

3:9132 ***β*-Chloroisobutyric acid**
— *β-Chloro-isobutyramide: cryst. from pet.* ether/EtOAc, m.p. 102–104°. [From *β*-chloroisobutyronitrile by partial hydrolysis with H_2SO_4: see reference (3) under 3:0235 (above).]

3:9295 **5-Chloropentanol-1**
(128) [illegible]
[illegible] ?.109, $n_D^{20} = 1.5169$;
[illegible]

3:9395 **6-Chlorohexanol-1**
(129) Preparation of $\bar{C}$ and its reactions with amines
K. N. Campbell, A. H. Sommers, J. F. Kerwin, B. K. Campbell, *J. Am. Chem. Soc.* **68**, 1557 (1946)

3:9567 **Phenylacetyl chloride**
(130) Friedel-Crafts reactions of $\bar{C}$ with anthracene, phenanthrene, or pyrene
Hoi, Royer, *Bull. soc. chim.* **1946**, 659–661; *C.A.* **41**, 3453 (1947)

3:9858 ***n*-Dodecanoyl chloride (lauroyl chloride)**
(131) Preparation of $\bar{C}$
Ackley, Tesoro, *Ind. Eng. Chem.* **18**, 444–445 (1946)
(—) See reference (116) under 3:7065 (above)

3:9865 **1,1,1-Trichloro-2,2-*bis*-(*o*-chlorophenyl)ethane ("*o,o'*-DDT")**
(132) Preparation of $\bar{C}$
Gätzi, *Helv. Chim. Acta* **29**, 1159–1163 (1946); *C.A.* **41**, 114–115 (1947)
(133) Isolation of $\bar{C}$ from technical DDT
Cristol, Soloway, Haller, *J. Am. Chem. Soc.* **69**, 510–515 (1947)

3:9885 ***n*-Tetradecanoyl chloride (*n*-myristoyl chloride)**
(—) See reference (116) under 3:7065 (above)

3:9960 ***n*-Octadecanoyl chloride (*n*-stearoyl chloride)**
(—) See reference (116) under 3:7065 (above)

are also present, a compound is said to belong to a higher order: e.g., compounds of carbon with both hydrogen and nitrogen, with oxygen and nitrogen, or with hydrogen, oxygen, and nitrogen comprise Order 2. A systematic arrangement of still higher orders has been developed but need not be fully amplified here.

The substance of the present volume is concerned primarily with compounds of Order 3, i.e., with compounds containing carbon and chlorine; carbon, oxygen, and chlorine; carbon, hydrogen, and chlorine; or carbon, hydrogen, oxygen, and chlorine. To all such compounds deemed of sufficiently general interest to warrant detailed treatment in this book, serial numbers have been assigned as later explained. Although such serial numbers are thus restricted to species of Order 3, a vast number of compounds belonging to other orders inevitably occurs in the course of the individual texts so that this volume has far wider utility than might at first glance be supposed. At the same time not all substances belonging to Order 3 are given numbers since many are not of sufficient value to warrant such extensive treatment.

2. The matter of suborders

In the general plan of ordinal classification, it is sometimes (but not always) useful to effect subdivision of orders into two suborders according to whether or not the pure compounds are colored. For both Orders 1 and 2, such subordering has special merit. For the present Order 3 compounds, however, the proportion of colored individuals is almost negligible, and employment of suborders has been avoided.

3. The arrangement of compounds of Order 3 into *divisons*

Just as the individual compounds of Order 1 were ultimately further subclassified into various *genera*, each characterized by a common behavior in certain prescribed and carefully defined *generic tests*, so it would of course be perfectly possible to set up an analogous series of genera for any or all of the higher orders. After considerable reflection and experimentation, however, such extension of the method of generic subclassification has seemed an extravagant formality whose added value for the higher orders does not warrant its establishment. Consequently, the individuals comprising the present Order 3 are not arranged by genera, and there are no standardized generic tests to be systematically applied.

Instead of arrangement by genera, therefore, the compounds assigned serial numbers in this book are arranged in three *divisions*. The first of these divisions comprises members of Order 3 which, when pure, are normally solids with at least reasonably definite melting points. The second comprises members of Order 3 which, when pure, are liquids with boiling points attainable and recorded at ordinary pressure. The third division comprises

members of Order 3 which, even when pure, are liquids which either cannot be distilled at atmospheric pressure without serious decomposition or for which such data are available only under reduced pressure. Ample cross-references connecting the solid and liquid divisions facilitate recognition of appropriate cases.

4. The sequence of compounds within the three *divisions*

DIVISION A. *The individual solids constituting Division A are arranged* in the order of increasing magnitude of their respective melting points. For compounds on which there is poor agreement regarding the true melting point, the value determining the position of the compound relative to its neighbors is not necessarily the highest listed. Values printed within square brackets have been regarded by the author on the collateral evidence as possibly doubtful, and such constants have been discounted in assigning positional sequence to the compound.

DIVISION B. This division, comprising liquids of Order 3 with boiling points at ordinary pressure, is (unlike either its predecessor or successor) further subdivided into two sections according to the specific gravity at 20°C. referred to water at 4°C. Section 1 contains such liquids with values of D_4^{20} greater than 1.15; Section 2 contains correspondingly those liquids for which the value of D_4^{20} is less than 1.15. Within each of the sections of Division B the individual species are arranged in the order of increasing magnitude of their respective boiling points, preferably at 760 mm. pressure. For compounds whose boiling points at this standard pressure are unreported, no attempt has been made to calculate over since to do so seems likely to introduce serious uncertainties.

DIVISION C. This division contains all serially numbered compounds of Order 3 *which have not been allocated to either of the preceding divisions,* such cases usually comprising liquids for which boiling points are reported *only* at reduced pressures. Within this division an entirely different method of establishing the listing sequence is employed; viz., the compounds are listed in ascending sequence according to the composition of their empirical formulas. For any given number of carbon atoms, compounds containing *carbon and chlorine, or carbon, oxygen, and chlorine, or carbon, hydrogen,* and chlorine, or carbon, hydrogen, oxygen, and chlorine fall in that sequence. Within any one of these four subgroups the sequence is determined by increasing magnitude of the number of component atoms in the sequence (as above) of carbon, hydrogen, oxygen, and chlorine. Although expressed in words this sounds formidable, even casual inspection of the Tables or of the Empirical Formula Index quickly supplies convincing evidence of its complete simplicity in actual practice.

5. The arrangement of data on individual compounds

Whether the amount of data for the compounds comprising this volume is large or small, and irrespective of numerous variations of details, a certain standard form may be recognized as common to all. This form may be construed as made up of the following five elements:

A. The heading.
B. Fundamental physical constants.
C. General data on other constants, preparation and properties.
D. Designation of special or preliminary tests.
E. Derivatives.
F. References to the original literature.

The relative amount of space devoted to these five aspects varies according to circumstances. Each is discussed below in much further detail.

A. *The heading*

The heading of each numbered compound comprises (in its most general form) five components which always occur in the following sequence from left to right, viz.,

1. Location number of compound in this book (Order 3)	2. Name (or names)	3. Structural formula	4. Empirical formula	5. Beilstein reference

(1) *The location number.* Each compound on which detailed treatment is given in this book has been assigned an arbitrary number to facilitate frequent cross reference in indexes and other parts of the text. This number consists of a digit representing the order of the compound (thus all species of this volume have location numbers beginning with 3), followed by a colon and then a four-digit arbitrary number. The system is, therefore, entirely comparable to a telephone number, the initial digit preceding the colon corresponding to an exchange, the four following digits corresponding to an individual line.

In assigning serial location numbers to the various individuals treated in this book, a principle has been maintained whose recognition greatly facilitates recognition of the physical nature of the corresponding substances. All members of Division 1 (solids) carry numbers between 1 and 4999; all members of Division 2, Section 1, are between 5000 and 6999; all members of Division 2, Section 2, are between 7000 and 8999; all members of Division 3 are between 9000 and 9999.

For a given compound, the full descriptive data are recorded only in one place, i.e., in that corresponding to the location number. When occasion

arises to be reminded in some other portion of the book of certain properties of a given compound, the *heading only* is repeated followed by a cross reference to the place of detailed description, the section usually occupied by the location number being indicated merely by a dash. The most frequent occasion for this type of cross reference is to indicate the boiling point of a compound normally met with as a solid, or alternatively the melting point of a substance normally met as a liquid.

(2) *The name (or names) of the compound.* The second element of the heading is devoted to the name (or names) of the compound. Out of all possible names, one (regarded for the purposes of this book as the "principal name") has been printed in bold-face capitals.

In many instances, however, this principal name is followed in ordinary type by one or more other names which are in common use and which might occur alternatively to users of this volume. All these names are appropriately entered in the alphabetical name index so that the location number is readily obtained irrespective of which name may be sought by the user.

(3) *The structural formula of the compound.* Since it is frequently easier to interpret the chemical reactions of a compound by contemplation of its structural formula rather than its name, such structural pictures are given for all compounds in this volume.

If a particular compound reacts as if it had two different structures, both are pictured.

Although such structural formulations are construed as the third element of the heading of each compound, it may happen that, owing to practical space considerations, the picture is not actually printed as part of the top line but depressed somewhat below it.

(4) *The empirical formula.* The fourth element of the heading is the empirical formula. This will be found useful in many ways, particularly in suggesting (especially with the amplification afforded by the empirical formula index) isomeric compounds from which distinction must be made, and in searching the abstract periodicals for data reported after the publication of this volume.

(5) *The Beilstein reference.* Each compound listed in these *Tables* carries in the upper right-hand corner as the fifth element of the heading reference to Beilstein's *Handbuch der organischen Chemie.* All such references designate the fourth edition of this important tool.

At the time of preparation of these *Tables*, all twenty-seven volumes of the primary series (covering the literature up to 1910) together with the corresponding twenty-seven volumes of the first supplementary series (1910-1919, inclusive) of Beilstein's *Handbuch* were available. For every numbered compound of these *Tables* which appears in either the main or first supple-

mentary series, the Beilstein reference will comprise two parts, the first giving the volume and page in the main series, the second giving corresponding reference to the first supplementary series. To distinguish the latter, the volume reference carries the subscript 1, and the page reference is placed between parentheses to indicate that the regular pagination of such supplementary volume is designated.

In addition to the main and first supplementary series of Beilstein mentioned above, there were also available during the preparation of these *Tables* the first five volumes of the second supplementary series (1920–1929) of Beilstein's *Handbuch*. For such of the present numbered compounds as were treated in this available fragment, the Beilstein reference will, therefore, contain a third element representing the volume and page involved. For this kind of case the volume reference bears the subscript 2 (to indicate second supplementary series) together with the page reference in parentheses as before.

In accordance with the above explanation, a given compound will have either two or three Beilstein references. It is, of course, possible for a compound to have citation to only one or two out of the three maximum possibilities; absence of any data for a particular Beilstein unit is indicated by short dashes after the volume number.

The remaining possible case is that in which the compound in question is of such recent origin that Beilstein contains no reference to it either in the main section or either supplementary series. Many such compounds occur in this Order 3. Under these circumstances the usual Beilstein citation is replaced by the Beilstein System Number of the compound, e.g., Beil. S.N. 644. Such type of reference immediately indicates that no reference to the substance is contained in any Beilstein issues through Vol. V of the second supplementary series. Whenever third, fourth, or later supplementary series become available, however, this system number will indicate the position of the compound within narrow limits, even though volume and page cannot now be predicted.

The practice of giving all three Beilstein citations wherever possible serves as a continual reminder that to look merely in the main series volume of Beilstein yields material only up to 1910; for the next two decades the corresponding first and second supplements must also be examined. In this respect these *Tables of Order* 3 extend the practice of those of Order 1, where only the main series citation was made, extension to the first supplement being left to the user.

That these references to Beilstein's *Handbuch* are here included only as an additional convenience to users of these *Tables* should be clearly understood. This book is wholly independent of Beilstein, and those users to whom Beilstein may be inaccessible are reassured that the value of these *Tables* to them is in no way impaired.

B. Fundamental physical constants

The five components of the standard heading having been discussed, some comment upon the next element of each description is required. This next element comprises what are here designated as "fundamental physical constants" and which in the most general cases consist of data on (1) the melting point, (2) boiling point, (3) density, and (4) refractive index. In the sequence named, these are arranged in four vertical columns from left to right of a given page. For substances which are solids under ordinary conditions, the melting-point column is the first at the left of the page with the boiling-point column next following in the left central section. For such solids only rarely will density or refractive index data appear. For liquids, however, the first left-hand column is devoted to boiling-point data, the melting points being displaced to the next right-hand column because of their subordinate value in such instances.

(1) *The melting point.* Whereas in the earlier *Tables of Order* 1 the general practice was to express only a single figure for this constant, the individual descriptions of this book include substantially all values that have been reported. However, values which in the light of collective subsequent results are certainly too low, or those which because of their wide range make no claim to accuracy, are omitted. The survey of values thus set forth, together with the fact that the source of each value is also given, permits the user to form his own opinion concerning the magnitude, degree of concordance, and precision of the available data.

For each individual compound the several values are arranged in the order of diminishing numerical magnitude. In general the value of highest magnitude is employed to determine the place of the individual solid relative to its fellows (i.e., to determine its serial location number). However, values enclosed by square brackets are regarded by the author on collateral evidence as being abnormally high, and such constants are ignored in establishing the serial number of the individual.

The several melting points are recorded here just as they are reported in the original literature; whenever the designations *corrected* or *uncorrected* were included in the original source, they are repeated here; most of the values, however, fail to specify whether they are corrected or not. This careless usage of much journal literature is to be deplored.

No attempt has been made in this book generally to maintain a distinction between melting point and freezing point. Undoubtedly, most of the values reported represent conventional capillary-tube melting points; frequently, however, the values are expressed to a degree of precision suggesting that a cooling-curve method was employed. Whenever the distinction is of importance, the user can readily ascertain full details from the cited references.

(2) *The boiling point.* In complete analogy with its treatment of melting points, the individual descriptions of this book include substantially all recorded values of the boiling point. These are tabulated in the order of diminishing numerical magnitude of the prevailing pressures. Wherever the data can be found, the value at 760 mm. pressure is cited; however, if this is not directly reported, no attempt has been made to convert the available figures over to that pressure, as to do so would introduce unwarranted assumptions. Values of the boiling point at various pressures are meticulously included in the *Tables*. However, when a careful physicochemical study has been made of the vapor pressure of an individual, selected values are printed and reference made to the original for further detail.

Even a casual examination of the boiling point data reported in this book leads at once to the conviction that there has been a great variation in the precision of measurement of the prevailing pressure over the boiling liquid. In fact an incredible proportion of workers has not reported any pressure figures at all or complacently referred to the "prevailing atmospheric pressure." Even when pressure measurements are reported, the evident general lack of concordance becomes distressing evidence of the inadequacy and inaccuracy of many of the data in the literature.

(3) *Densities.* Unlike the extensive treatment accorded for melting points and boiling points, this book does not attempt to tabulate all possible published values for the densities of liquid compounds. However, all available data for density at 20°C. referred to water at 4°C. are given; and, whenever possible, the same procedure is extended to values for D_4^{25} and D_4^{15}. Note that, when values are given for various temperatures, those for the highest temperature are printed at the top of the density column, followed in diminishing magnitude of temperature by the other values. This simple and obvious device is intended to assist users of these *Tables*, but they should be reminded that this plan was not (unfortunately) employed with the *Tables of Order* 1.

Density data are given for all liquids for which they can be found; for compounds normally solid, the density is occasionally given for some temperature above the melting point, especially if refractive index values at the same temperature are also available.

Whenever in an original paper there exists any uncertainty as to the temperature of the water with which comparison is made, the lower subscript is replaced by a short dash to indicate that the omission of this figure is not accidental but is because of inadequate expression in the original. In many or even most such cases it is possible that the author intended to convey that the density was expressed with respect to water at the same temperature. This author, however, declines to make any such assumption and ventures to express the view that research workers and journal editors should insist upon unambiguous expression of such data.

(4) *Refractive indices.* These are usually given in the form n_D^{20}, i.e., the refractive index determined at 20°C. with the D line of sodium light. In some instances data for other lines of the spectrum have been reported here when no data on the D line were available. As with the densities above, refractive index data are frequently printed for other temperatures, and the same typographical convention of placing the higher-temperature values above the lower-temperature ones is continued.

C. General data on other constants, preparation, and properties

The preceding details of the five components of the heading and the four so-called fundamental constants having been discussed, it is now desirable to comment upon the third element of the text of each compound. The material comprising this third section actually comprises most of the space of this book. Although sometimes consisting of only a few paragraphs, there are many members of Order 3 for which the general exposition of behavior requires many pages. Such extended treatments are frequently (although not invariably) subdivided by major and minor headings intended to facilitate quick recognition of the probable location of particular types of desired information. Careful examination of the text of any typical individual compound will quickly disclose that it has in general been dealt with in generous fashion. At the same time it is obvious that a line must be drawn somewhere. For example, in connection with the discussion of an alkyl halide such as *n*-butyl chloride, it is certainly of highest relevance to indicate the mode and extent of its ability to form *n*-butyl magnesium chloride. Furthermore, the value of the simpler reactions of the RMgCl compounds, particularly with reference to their utility in the identification of the initial halide itself, is evident, but on the other hand no attempt has been made to cover all the known reactions of butyl magnesium chloride since that would involve an undertaking of disproportionate magnitude.

Although details of the texts of individual compounds naturally differ in nature and magnitude and are influenced by the literature content corresponding to the direction of published research, certain aspects occur with sufficient frequency to warrant comment.

The text of each compound invariably comprises its methods of preparation and its chemical behavior. For many of the more common or especially important species, these two aspects are often preceded by an introductory section containing certain physical data (in addition to that of the heading) likely to be of particular interest or utility to organic chemists. Examples of such entries include binary and ternary systems with other compounds, especially with reference to freezing-point composition data, azeotropes, densities and/or refractive indices, etc. In this introductory section also attention is frequently directed to methods of quantitative determination

of the compound, examples of industrial or other utilization, biochemical behavior especially with regard to studies on toxicity, antiseptic character, etc. The selection of entries for this introductory section is admittedly arbitrary, and users are reminded that this book makes no claim to include all known data even on the compounds to which serial numbers are assigned. Indeed, in an effort to keep the volume within reasonable bounds, certain types of data of value to organic chemists have been deliberately (though regretfully) excluded, such as references to absorption or Raman spectra, dipole moments, and viscosities, although many instances of the four fundamental physical constants of the heading are drawn from original publications primarily concerned with these aspects.

Within the text of each individual numbered compound (immediately following the above-mentioned introductory section, if any), there occurs a section on its methods of preparation. This treatment has purposely been made as complete as possible. To a limited degree distinction has been made between preparation and formation; but, because even in contemporary publications many authors fail to report yields, adequate recognition of the appropriate category is not always possible. Original results reported only in terms of weight have been calculated over to percentage yields. Variations in yields by a single method of preparation are contrasted by massing them in the text, the uniform practice of following each statement with its corresponding citation serving conveniently to associate each yield with a particular modification. With compounds for which there are many modes of preparation, the most generally practicable methods are often singled out for particular mention at the beginning of the preparative section, followed by a systematic presentation of all the recorded methods under various subheadings appropriate to the circumstances.

Users of this book will find these sections on preparation not only extremely useful from the viewpoint of comparison of various alternatives but also very stimulating and suggestive in the formulation of unconventional approaches to their particular problems.

Within the text of each numbered compound of this book, following the introductory section (if any) and the preparative section, is next set forth the significant aspects of its chemical behavior. The length of this part of the treatment varies widely from a few phrases to many pages. Very long treatments are appropriately subdivided for practical convenience, the particular sequence of arrangement being dictated by various circumstances. For example, the earlier subdivisions often deal with pyrolysis, reduction, oxidation, and substitution reactions, followed by the behavior with inorganic and organic reactants. With bifunctional compounds the initial group is frequently followed by the behavior of each function with inorganic and organic reactants in that order. Users will experience no difficulty in recognizing

the systematic organization of each compound. Emphasis has been placed upon a systematic and logical presentation of each case, and the above general outline has served the construction of this book only as a general guide rather than a rigid frame.

Two matters continually arising within the descriptive text deserve a further word of comment. The first relates to the fact that, in the course of reporting the chemical behavior of each numbered compound, there is necessarily involved reference to many other substances. Such of these as appear in either this volume (Order 3) or its predecessor (Order 1) are immediately followed by their serial numbers. A great many other compounds belonging to orders not yet written up in this series are inevitably involved; for such compounds reference to Beilstein is usually made for the convenience of the user who may have occasion to follow the matter further.

The second matter involves the practice of this book with respect to citations. Many instances appear which at first glance might appear to involve unnecessary repetition of the citation number, but which really comprise signals to the reader. As a simple illustration, consider the following extract from the text of *p*-chlorophenol, referring to the method of preparation of its *N*-(*m*-nitrophenyl)carbamate, viz.: "From $\bar{C}$ with *m*-nitrobenzazide (283) or *m*-nitrophenyl isocyanate (283) in lgr. (283)." This usage designates the fact that the preparation of both the *m*-nitrobenzazide and the *m*-nitrophenyl isocyanate is given in reference (283) together with their utilization as reagents in the conversion of *p*-chlorophenol to the corresponding *N*-(*m*-nitrophenyl)carbamate. Of course, with commonly available reagents such extra citations need not be included.

In view of the nature and magnitude of the text of this book, there may be a tendency to regard it as a specialized *Beilstein* within its field. Such a characterization would carry the implication that the text comprises all known chemical information with respect to each component compound, whereas only the more important representatives of such data are offered. In this connection one common misunderstanding with respect to Beilstein's *Handbuch* has significance. The Beilstein classification employs the principle of "latest position in the system." This means that, when a given fact could logically be placed in several different places, it is in general associated with the last of such places in the systematic plan. For example, as the methyl ether of phenol, anisole could conceivably be discussed either under methyl alcohol or under phenol. Following the above principle, however, Beilstein discusses it under phenol with no mention whatever under methyl alcohol. For Beilstein's purpose this principle is extremely well founded, results in an orderly, systematic, and uniform procedure, and, if properly understood, causes no trouble to the user. Its employment does have the unfortunate result, however, that for compounds occurring early in the

systematic sequence the impression is often given to the uninitiated that nothing is known about reactions involving components themselves listed later in the classification scheme. In contrast to the above Beilstein usage, the present *Tables* are unrestricted by any such arbitrary rule. Inasmuch as a large proportion of the compounds with which it deals are those which in the Beilstein classification appear to be inadequately described because of their earlier position in the sequence, users will quickly appreciate the added convenience of a generous treatment of the chemistry involved.

D. Preliminary tests

For certain of the more common compounds included in these *Tables*, there exist specific or semi-specific color tests. These are generally simple to execute, may often be applied satisfactorily to minute amounts of material, and, when positive, are so significant that their trial, if indicated, should invariably precede the derivatization of the sample. Such tests are indicated by the symbol Ⓟ but should be regarded as merely preliminary in character and not always carrying the same conviction as the derivatives.

E. Derivatives

The text section of each numbered compound is usually concluded by a group of derivatives. Those which for one reason or another have special importance are designated by the symbol Ⓓ placed at the left-hand side of the page. Interspersed with such cases will frequently be found others not bearing this symbol but instead merely designated by a dash. Relatives of the original parent compound so designated comprise materials, knowledge of whose existence (or less commonly nonexistence) or properties may be needed for comparison with related cases for the particular parent or other isomers thereof. Wherever possible, specific data on each relative included in this derivative section are given; in many cases, however, where careful systematic search has failed to uncover any published record of the compound, it is characterized in these tables as "unreported." All chemists recognize that reliable information that a particular compound has not yet been reported is more to be desired than its complete omission; and this feature of this volume will effect substantial economies of time for its users. Naturally, as time goes by the constant publication of new data will enable some of these informational gaps to be filled.

More than one value for the melting point of a particular product derived from a numbered parent or, conversely, several citations for the same value will often be noted through all parts of this book. These practices serve, respectively, to suggest caution because of lack of agreement and to attract attention to the concordance of results of several different workers.

The sequence in which these derivatives are listed has no relation to their

respective merits as means of identification of the particular parent. For each class of compounds, the particular sequence is arbitrary but standard in form and sequence in order to facilitate intercomparison and easy reference. For any particular class, however, the sequence is similar to that employed in Order 1 for the corresponding nonchlorinated parent.

F. Literature references

The fifth and final section of the descriptive material comprising each serially numbered compound comprises the corresponding references to the chemical literature. These are associated with the corresponding portions of the descriptive text by arbitrary numbers set in bold-face carets, e.g. **(5)**, the journal names being uniformly represented by the standard abbreviations employed by *Chemical Abstracts*. The single exception to the use of *Chemical Abstracts* abbreviations for literature references is that the German journal recently known as *Chemisches Zentralblatt* (but formerly as *Chemisches Centralblatt*) is here designated as *Cent.* This convention adequately suggests the name of the periodical in less space and improves the corresponding Beilstein abbreviation (C.) by avoiding confusion with Centigrade temperature.

The total number of such literature references in this book is very large, owing in part to the greatly increased scope of this Order 3 as compared with the restricted treatment of compounds of Order 1. It will be observed that, in addition to a much fuller record of the four fundamental physical constants, and a more generous regard for a diversified array of derivatives, this book (unlike its predecessor) deals extensively with the preparation and chemical behavior of its component species. Furthermore, whereas the earlier book arbitrarily excluded references to the patent literature, the present volume not only permits their inclusion but draws rather heavily upon it. The rapid growth of industrial organic chemistry, the fact that numerous chloro compounds of Order 3 represent individuals of great industrial significance, and the circumstances that for many such cases a large proportion of the available information is of such recent origin that little of it can be found in conventional monographs or other compendia have combined to necessitate considerable emphasis on the technical literature.

For a given individual numbered compound, a particular published article or patent is listed *only once*. The citation number representing the reference may be given many times in the descriptive text, but in the literature reference section the reference itself is not repeated. On the other hand, a given original article covering several individual compounds included in this book will be cited under each of the materials to which the article is relevant.

The order in which the literature references are arranged is determined by the sequence in which necessity for their mention arises in the text. This

results, of course, in what may appear to be a random sequence. The author is well aware that rearrangement of these references into a sequence comprising an alphabetical author index is possible. Such an operation, however, has been regarded as impracticable since it would multiply severalfold the opportunity for error and would be unlikely to confer advantages commensurate with the labor involved.

Literature references to journals considered to be generally accessible are given directly; but those to articles in journals with limited circulation or to articles in languages other than English, German, French, or Italian are usually accompanied by the location of the corresponding abstract in both the *Chemisches Centralblatt* and the *Chemical Abstracts*. This leads to the suggestion that users of this book, to whom a particular primary publication may be inaccessible, may themselves locate the corresponding abstracts by means of the usual Author Indexes to these works. Consultation of the abstract must never be regarded as equivalent to examination of the original publication but is generally better than no information at all.

Citations to original articles in scientific journals often refer to individual pages but sometimes also to a spread of pages, depending upon the nature of the article. The practice so frequently employed by others of citing an article merely by giving its initial page and leaving to the reader the often laborious job of locating the individual page germane to the aspect in question is deplored by the present author and has been avoided in this book. When a page spread (occasionally extending to the whole of a particular article) is cited, the reason is usually that the construction of the original paper is such that relevant material is scattered throughout the paper and individual page citation might be not only inadequate but even misleading. Since a given article appears (in general) but once in the group of literature references associated with each numbered compound, however, and since therefore the single number representing it may be used many times during the various aspects of the corresponding text, users finding that one of several individual pages so cited is inapplicable will recognize it is to be associated with some other aspect elsewhere in the text.

Attention is called to certain advantageous and unique practices followed by this book in connection with its citations of patents. The first element of patent citation is the name of the inventor (or of all, if more than one) if this information is known. The second element comprises the name of the company to which the patent has been assigned. All American patents are required by law to be issued to the inventors but are commonly assigned to the sponsor of the work. Foreign patents, however, do not always carry the names of individual inventors; in that event the company name has to serve both purposes. The third element is the nationality and number of the patent accompanied by its date of *issue* (not application). The fourth

element comprises reference to abstracts of the patent both in the *Chemisches Centralblatt* and in *Chemical Abstracts.* There are three reasons for this multiple form of abstract reference.

The first is that few chemists have immediate access to the corresponding original patents themselves and appreciate the convenience of the abstract. The second is the plain fact that the patent abstracts published by the *Chemisches Centralblatt* are usually so much more descriptive and more nearly complete than those of *Chemical Abstracts* that many chemists prefer to use the former. Doubters of this difference of quality between the two abstract journals are invited to convince themselves by direct comparison. Finally, the *Chemical Abstracts* reference is also included, however, because there may be some users of this book to whom the *Centralblatt* may not be available or who are timid about their ability to read even technical German. If in a particular case the patent has not been abstracted at all, this fact is also noted. Furthermore, because of the present inaccessibility of more recent issues of the *Centralblatt*, it has been necessary in some of the more recent references to cite only *Chemical Abstracts.*

In connection with the citation of patents, many instances will be noted in which the reference includes also the equivalent patents of other countries, each of these being accompanied by its dates, abstract references, etc., as for an individual patent.

The reader's attention is directed to the obvious fact that many patents are expressed in general terms so that, even though the protection sought may frequently cover one or more of the component compounds of this book, the specific individuals are not mentioned by name. No attempt has been made to interpret such general patents. For this reason systematic searchers will often consult higher or lower homologs of the compound comprising their initial interest.

6. Abbreviations

Necessity for economy of space has required in this book a continuation of the extensive set of abbreviations used with the earlier *Tables of Order* 1 together with certain additions required by new circumstances. All these abbreviations have been selected so as to suggest the full word, particularly when assisted by the context. No attempt has been made to enslave the text to the abbreviations, however, and the full word is sometimes employed even though a mnemonic for it is given in the *Table of Abbreviations.*

7. Indexes

This book contains five different types of indexes; three of these are distinctly novel and two are conventional, as explained below.

A. The empirical formula index

The index of empirical formulas lists each of the compounds in this book in the conventional familiar form under one or another of four parts according to whether the particular compound contains (1) only carbon and chlorine; (2) carbon, oxygen, and chlorine; (3) carbon, hydrogen, and chlorine; (4) carbon, hydrogen, oxygen, and chlorine. Within each of these parts the individual empirical formulas are arranged in groups according to increasing numbers of carbon atoms, and for a given number of carbon atoms according to increasing numbers of the other component atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index (see below).

This empirical formula index contains also for each group of isomers both the molecular weight and the percentage chlorine content, each computed to one place of decimal units. This index not only serves as a convenient record of these constants but also suggests to the user isomers of the particular individual. The formula index may also be employed occasionally as a final verification of the presence or absence of a particular compound from the *Tables*, in possible instances where the names which occur to the worker do not appear in the alphabetical index.

A brief statistical analysis of this index may be of interest. The 1320 individual compounds comprising this book are distributed among 366 groups of isomers as follows:

		Groups of Isomers	Individuals
Part A	C/Cl compounds	11	11
Part B	C/O/Cl compounds	18	21
Part C	C/H/Cl compounds	135	566
Part D	C/H/O/Cl compounds	202	722
	Total	366	1320

The minimum number of isomers for a given empirical formula is obviously one; 28 of the above 366 groups represent such minimum cases. The maximum possible number of individual compounds within a particular empirical formula is, of course, indeterminately large; however, it is of interest to note that, of the 366 groups of isomers in this book, the largest number of individual compounds (21) occurs for the empirical formula $C_8H_7O_2Cl$. Other formulas with substantial numbers of individuals comprise $C_5H_9O_2Cl$ with 20, $C_7H_{15}Cl$ and $C_8H_{17}Cl$ each with 18, $C_5H_{10}Cl_2$ with 17, and $C_6H_{11}Cl$, $C_6H_{13}Cl$, and C_8H_9OCl each with 16, corresponding to a particular molecular weight.

B. Index of empirical formulas by percentage chlorine content

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of diminishing percentage of chlorine. This

type of index is unique; nothing of this sort exists in any other publication so far as is known. Many uses of such an index will suggest themselves, the most obvious example being to suggest various empirical formulas corresponding to a particular chlorine content.

Within this index will be observed many examples of identical chlorine contents for several different formulas; e.g., a percentage chlorine of 37.5 is common to the four different formulas $C_2H_3O_2Cl$, C_3H_7OCl, $C_8H_6OCl_2$, and $C_{14}H_9Cl_3$, despite the fact (as seen from the Empirical Formula Index) that the molecular weights of the last two are quite different from the others.

C. Index of empirical formulas by molecular weights

This index lists the 366 empirical formulas of the numbered compounds contained in this book in order of increasing magnitude of molecular weight. This index (like the preceding one) is unique, and nothing of the sort exists in any other publication so far as is known. Many uses of this index will suggest themselves, the most obvious example being to suggest various empirical formulas having the same molecular magnitude.

Within this index will also be observed many examples of identical molecular weights for several different formulas; e.g., the molecular weight of 136.6 is common to the three different formulas $C_5H_9O_2Cl$, $C_6H_{13}OCl$, and C_8H_5Cl.

D. Index of compounds according to chemical types

Since, as more fully explained earlier in this chapter, the component individuals of this book are not arranged in arbitrary genera and no standardized generic tests comparable to those of Order 1 have as yet been developed, the inclusion in this volume of an index in which the compounds are arranged according to the chemical classes to which they belong is of special value and utility.

In this chemical-type index, each compound is listed in at least one of eight chemical classes (units) as follows:

Unit 1. Chloro substitution products of saturated acyclic hydrocarbons.
Unit 2. Chloro substitution products of unsaturated acyclic hydrocarbons.
Unit 3. Chloro substitution products of cyclic hydrocarbons.
Unit 4. Chloro substitution products of hydroxy compounds (alcohols or phenols).
Unit 5. Chloro substitution products (and their relatives) of carbonyl compounds (aldehydes, ketones, quinones, aldehyde polymers, acetals, alcoholates, etc.).
Unit 6. Chloro substitution products of carboxylic acids and anhydrides.
Unit 7. Acyl chlorides.
Unit 8. Chlorine substitution products of ethers and of esters.

Compounds of the last five units containing more than one functional group are also listed under such of the others as may be appropriate. For example, 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 is listed both as a

carbonyl compound (Unit 6) and as a phenol (Unit 4); diethylene glycol mono(chloroacetate) is listed not only as an ester (Unit 8) but also as an alcohol (Unit 4) and an ether (Unit 8).

It may be of interest to summarize briefly the distribution of the compounds in this book among the several classes as shown in the following summary:

Unit 1	221	Unit 5	146
Unit 2	182	Unit 6	137
Unit 3	174	Unit 7	142
Unit 4	211	Unit 8	182

The total number of such unit listings (1395) thus exceeds the number of individual compounds (1320) by an amount representing the cases of multiple functions.

E. Alphabetical Index

This conventional type of index includes not only the " principal " name, but also all the subsidiary names given in the *Tables* for every numbered compound in this book. It cannot, of course, guarantee to contain every name which might conceivably be applied since, for the field of chemistry, such names are legion. However, with every name that is listed is associated the corresponding location (or serial) number, so that use of this index is perfectly straightforward and the index requires no cross referencing within itself. The first letter of the first syllable of the name proper establishes its position in the alphabetical sequence irrespective of any literal or numerical prefixes such as *o*-, *m*-, *p*-, *sec*-, *ter*-, *cis*-, *trans*-, α-, β-, γ-, δ-, *d*-, *l*-, *meso*-. Within a particular group of isomers with the same name, however, the sequence is *o*-, *m*-, *p*-; *sec*-, *ter*-; or α-, β, γ-, δ, etc. Iso is not construed as a prefix but as part of the main root. Further details of this sort are given in the introduction to the index itself.

CHAPTER II

DIVISION A. SOLIDS

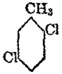
(3:0000–3:0499)

— PENTACHLOROACETONE $Cl_2CH—\underset{\underset{O}{\|}}{C}—CCl_3$ C_3HOCl_5 Beil. I - 656 / I_1— / I_2—

M.P. $+2.1°$ **B.P.** 192°

See 3:6205. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

— 2,5-DICHLOROTOLUENE



$C_7H_6Cl_2$ Beil. V - 296 / V_1— / V_2-(231)

M.P. 5° **B.P.** 199° at 761 mm. $D_{20}^{20} = 1.2535$

See 3:6245 *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

— *p*-CHLOROTOLUENE

C_7H_7Cl Beil. V - 292 / V_1-(150) / V_2-(226)

M.P. $+7.8°$ **B.P.** 162°

See 3:8287. *Division B: Liquids, Section* 2, $D_4^{20} < 1.15$.

— 1,1-DICHLORO-2-METHYLPROPANOL-2 (*unsym.*-Dichloro-*ter*-butyl alcohol; dichloromethyl-methyl-carbinol) $CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}—CHCl_2$ $C_4H_8OCl_2$ Beil. I - 382 / I_1— / I_2—

M.P. $+8°$ **B.P.** 151° $D_4^{19} = 1.2363$ $n_D^{19} = 1.4598$

See 3:5772 *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

— *o*-CHLOROPHENOL

C_6H_5OCl Beil. VI - 183 / VI_1-(98) / VI_2-(170)

M.P. 8.0° **B.P.** 175–176° $D_4^{25} = 1.2456$ $n_D^{25} = 1.5573$

See 3:5980. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

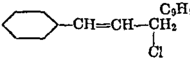
— DI-(β-CHLOROETHYL) CARBONATE $C_5H_8O_3Cl_2$ Beil. III — / III_1— / III_2-(5)

$(ClCH_2CH_2O)_2C=O$

M.P. 8.5° **B.P.** 240–241° $D_4^{20} = 1.3506$ $n_D^{20} = 1.4610$

See 3:6790. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

3:0010 CINNAMYL CHLORIDE (3-Chloro-1-phenylpropene-1)



C_9H_9Cl Beil. V - 482, V_1-(232), V_2-(372)

M.P.	B.P.				
8–9° (1)	140°	at 37 mm., sl. dec. (5)		$D^{25}_{-} = 1.08815$ (9)	$n^{25}_{D} = 1.58065$ (9)
8° (2)	125–126°	at 22 mm.	(6)	$D^{15}_{4} = 1.101$ (6)	$n^{12}_{D} = 1.587$ (8)
7–8° (3)	120°	at 18 mm.	(6)	$D^{12}_{4} = 1.090$ (8)	
4–9° (4)	117–119°	at 17 mm.	(7)		
	118°	at 15 mm.	(8)		
	115°	at 13 mm., sl. dec.	(5)		
	119.5–120.5°	at 12 mm.	(9)		
	116–117°	at 12 mm.	(1)		
	108°	at 12 mm.	(10)		
	106°	at 10 mm.	(11)		
	109–110°	at 6 mm.	(3)		
	102–103°	at 5 mm.	(3)		
	101.5–103.4°	at 5 mm.	(12)		
	94°	at 5 mm.	(13)		
	86–87°	at 2 mm.	(3)		

Care should be taken to avoid confusion of C̄ with the acid chloride of cinnamic acid; the acid chloride is properly designated as cinnamoyl chloride (3:0330); furthermore note that some of the older publications designate C̄ as "styryl chloride," which is now incorrect since in current usage the name *styryl* is reserved for the radical $C_6H_5.CH{=}CH$— derived from styrene (14).

Attention is also drawn to the fact (not fully recognized in the older work) that in some (but not all) reactions of C̄ the prods. obtained may in part be derived from the synionic mesomer of C̄, viz., phenyl-vinyl-carbinyl chloride (3-chloro-3-phenylpropene-1); for examples see below.

C̄ when pure is colorless oil with no odor of HCl; if HCl is present C̄ soon darkens on stdg. — C̄ should leave no residue on distillation, and best yields of RMgCl (see below) are obtainable only with freshly distilled C̄ (3).

[For prepn. of C̄ from cinnamyl alc. (1:5920) with HCl gas at 0° (yields: 92–93% (1), 78% (7), 60% (12)) (5) (6) (15), with HCl gas in CCl_4 soln. at room temp. (85% yield (7)), with 6–7 wt. pts. 6 *N* HCl on distn. (79% yield (4)), or with conc. HCl + $ZnCl_2$ in C_6H_6 (54% yield (16) see indic. refs.; from cinnamyl alc. (1:5920) with PCl_3 in C_6H_6 (62.5% yield (1)), or PCl_3 + $ZnCl_2$ in C_6H_6 (65% (16)) (note that PCl_5 + $ZnCl_2$ in C_6H_6 gave only tar (16)); from cinnamyl alc. (1:5920) with $SOCl_2$ + pyridine in $CHCl_3$ (yields: 83% (3), 69–75% (12)), with $SOCl_2$ + diethylaniline (18) or other tertiary bases (18), or with excess $SOCl_2$ in C_6H_6 (72% yield (16)) see indic. refs.; from cinnamyl ethers by cleavage with HCl (22° Bé) on htg. under press. see (8); from cinnamyl acetate (see below) by passing in dry HCl see (18).]

[For prepn. of C̄ from phenyl-vinyl-carbinol [Beil. VI-572, VI_1-(283)] (7) with HCl gas (7) (10) or with *p*-nitrobenzoyl chloride in ether on htg. in s.t. (10); from phenyl-vinyl-carbinyl acetate with HCl gas see (19).]

C̄ with Br_2 (1 mole) adds 2 atoms halogen yielding (20) (6) (10) α,β-dibromo-γ-chloro-*n*-propylbenzene, tbls. from ether, m.p. 104–105° (6) (10).

C̄ with conc. HI ($D = 1.7$) (3 wt. pts.) in AcOH (7) or C̄ with KI in dry acetone (11) gives in good yield (7) cinnamyl iodide, pale yel. lfts., which after very careful recrystn. from AcOH have m.p. 57° (7); note, however, that the substance is very unstable, cf. (7) (11).

[$\bar{C}$ on htg. with salts of acids yields a mixt. of the corresp. esters of cinnamyl alcohol (1:5920) and phenyl-vinyl-carbinol, the proportions of which vary with the nature of the acid radical, the metal, solvent, etc.; for extensive study of the reaction see (19) (7).] — [For behavior of $\bar{C}$ with ethyl sodioacetoacetate (21), Ag salt of 3-hydroxynaphthoquinone-1,4 (2), or with 1,5-dichloroanthrone + aq. KOH (22) see indic. refs.]

$\bar{C}$ readily hydrolyzes to the corresp. alc. (1:5920): e.g., $\bar{C}$ with aq. on boilg. for 1 hr. is 75% saponified (7); $\bar{C}$ with boilg aq. 1 *N* NaOH is 95% hydrolyzed in 1 hr. (7); note, however, that $\bar{C}$ is remarkably stable toward strong aq. alk. in cold (e g., with 3.5 vols. 53% aq. NaOH only trace of hydrolysis even after 8 hrs. shaking (7)); note also that the cinnamyl alc. (1:5920) obtd. by hydrol. is contaminated with di-cinnamyl ether, b.p. 231–232°, and probably also by the ether from phenyl-vinyl-carbinol. — $\bar{C}$ (10 g.) with excess cold dil. aq. Na_2CO_3 on shaking 85 hrs. gives phenyl-vinyl-carbinol (1.3 g.) + cinnamyl alc. (1:5920) (0.7 g.), di-cinnamyl ether (2 6 g.) + unhydrolyzed chlorides (4.1 g.) (7).

[$\bar{C}$ with *abs.* alc. KOH yields only (7) cinnamyl ethyl ether; note, however, that the course of the reaction is modified by pres. of aq. and that $\bar{C}$ with NaOH in 70% aq. alc. the cinnamyl ethyl ether is accompanied by 25–30% of ethyl phenyl-vinyl-carbinyl ether (7); furthermore $\bar{C}$ with silver oxide in *abs.* alc. (thus even in absence of aq.) gives *both* ethers (7) (for numerous details see (7)).]

[The behavior of $\bar{C}$ with NH_3 (or amines) is doubtless similarly influenced by the environment but has been less thoroughly studied. — $\bar{C}$ in ether with large excess conc. aq. NH_4OK on stdg. gives (77% yield (23)) tetracinnamylammonium chloride, ndls. from alc., m.p. 199° (23); $\bar{C}$ with abs. alc. NH_3 gives (24) (25) (5) mono-, di- and tri-cinnamylamines.]

$\bar{C}$ with tertiary amines forms quaternary salts. e g., $\bar{C}$ with Me_3N in abs. EtOH 24 hrs. at room temp. gives (26) (25) cinnamyl-trimethyl-ammonium chloride, very hygroscopic solid (for derivatives see (25) (26)); for quaternary salt formn. of $\bar{C}$ with dimethylaniline (15) or pyridine (6) (5) see indic. refs.

[$\bar{C}$ (1 mole) with aniline (4 moles) in ether as directed gives (50% yield (27)) *N*-(cinnamyl)-aniline, m.p. 21°, b.p. 200–202° at 12 mm., 178° at 3 mm. (27); $\bar{C}$ (1 mole) with hexamethylenetetramine (1 mole) in aq. alc. as directed gives (20–30% yield (8)) cinnamaldehyde (1:0245).]

$\bar{C}$ (freshly distilled) with Mg in dry ether under special conditions gives (83% yield (3)) (12) RMgCl: note carefully, however, that this Grignard is (or behaves as) a mixture consisting of 27% cinnamyl MgCl, C_6H_5—CH=CH.CH_2MgCl, accompanied by 73% phenyl-vinyl-carbinyl MgCl, C_6H_5—C(MgCl).CH=CH_2 (12).

[The reactns. of the Grignard mixture thus obtd. from $\bar{C}$ therefore generally yield prods. corresponding to both the components sometimes accompanied by material originating from coupling reactns. of RMgCl (either or both types) with itself: e.g., RMgCl (designating the above mixture) on acid hydrolysis with 3 *N* H_2SO_4 gives not only both propenylbenzene [Beil. V-481, V_1-(231), V_2-(371)], b.p. 176°, and allylbenzene [Beil. V-484, V_1-(233), V_2-(373)], b.p. 156° (from the two RMgCl types) (combined yield 47% (12)), but also a high-boilg. residue (81% yield (12)) (from coupling of RMgCl, see below).]

[$\bar{C}$ (2 moles) with Mg (1 atom wt.) in dry ether subsequently hydrolyzed gives a high-boilg. fractn. consisting of a solid and a liquid hydrocarbon: the solid hydrocarbon (8–9% yield (28)) (1) is 1,6-diphenylhexadiene-1,5 (dicinnamyl) [Beil. V_1-(338), V_2-(597)], lfts. from alc. or AcOH, m.p. 82° (1), 81–82° (29), b.p. 211° at 11 mm. (1), 180° at 5 mm. (29); the liquid hydrocarbon (42.9% yield (28)) has now been recognized (28) (contrary to earlier views (1)) as 1,4-diphenylhexadiene-1,5, b.p. 157–160° at 2 mm., $D_{20}^{20} = 0.9919$, $n_D^{20} =$ 1.5890 (28). — For mode of formation of these prods. see (28).]

[$\bar{C}$ converted to RMgCl (see above) and reacted with NH_2Cl at −20° gives (14% yield (33)) cinnamylamine.]

Ⓓ Phenyl-vinyl-acetic acid: cryst. from pet. ether at −10°, m.p. 23–24° (30). [From RMgCl with CO_2 (note that ord. method gives low yields (38% (3) cf. (17)) but simple modification of carbonation technique raises yield to 62–66% (3)).] — This acid on htg. or on warming with either alk. or acid isomerizes (by change in position of double bond) to α-phenylcrotonic acid (methylatropic acid) [Beil. IX-615)] (see also next paragraph).

—— α-Phenylcrotonic acid (methylatropic acid): pr. from alc., ndls. or lfts. from aq., m.p. *135–136° (17) (p-nitrobenzyl ester, m.p. 80–81° (31))* (see also preceding paragraph). [From RMgCl (above) with ethyl chloroformate (3:7295) followed by hydrolysis of the intermediate ethyl phenyl-vinyl-acetate by htg. with 20% HCl or by shaking for 2 days with alkali (the hydrolysis being accompanied by simultaneous rearr. of the unsatd. linkage) (30).]

Ⓓ *Phenyl-vinyl-acetic anilide: cryst. from C_6H_6, alc., or $CHCl_3$, m.p. 97–98° (30).* [From RMgCl (above) with phenyl isocyanate in dry ether (30); this prod. may be accompanied by a small amt. of α-phenylcrotonanilide, m.p. 192°, from partial isomerization during the reactn. (30).]

Ⓓ *N*-(Cinnamyl)phthalimide: cryst. from 90% alc. or 90% AcOH (24) or from *n*-PrOH *(32), m.p. 156° (32), 153° (24). [From C̄ with K phthalimide by htg. at 160° for* several hrs. (24); note that the structure of this prod. has been confirmed as the cinnamyl (and not the phenyl-vinyl-carbinyl) type (32).]

[illegible] 178 (1910). (2) Fieser, *J. Am. Chem. Soc.* **48**, 3213 (1926). [illegible] 1052–1055 (1931). (4) Norris, Watt, Thomas, *J. Am.* [illegible], Franke, *Arch. Pharm.* **247**, 333–334 (1909). (6) Klages, [illegible] 7) Meisenheimer, Link, *Ann.* **479**, 211–277 (1930). (8) Bert, Dorier, *Compt. rend.* **191**, 332–333 (1930); *Cent.* **1930**, II 2376; *C.A.* **24**, 5739 (1930). (9) Goebel, Wenzke, *J. Am. Chem. Soc.* **60**, 698 (1938). (10) Meisenheimer, Schmidt, *Ann.* **475**, 178–179 (1929). [illegible] (12) Young, Ballou, Nozaki, *J. Am. Chem.* [illegible] *Am. Chem. Soc.* **60**, 2005 (1938). (14) [illegible] (16) Clark, Streight, *Trans. Roy. Soc.* [illegible] (21) Bergmann, Corte, *J. Chem. Soc.* **1935**, 1304. (22) [illegible] *J. Chem. Soc.* **1935**, 1104. (23) Emde, *Arch. Pharm.* **249**, 93–103 [illegible] 1865 (1893). (25) Emde, *Arch. Pharm.* **244**, 271–277 ([illegible] *Pharm.* **243**, 75–78 (1905). (27) von Braun, Tauber, [illegible] *Chem. Soc.* **54**, 2072–2075 (1932). (29) [illegible] 46 (1931). [illegible] (1932). (32) Bergmann, *J. Chem. Soc.* **1935**, [illegible] **58**, 28 (1936).

—— **HEXACHLOROBUTENE-Y** $C_4H_2Cl_6$ **Beil. S.N. 11**

M.P. 9.5–11° **B.P. 125.5° at 25 mm.**

See 3:9050. *Division C: Liquids with b.p. only at reduced pressure.*

3:0013 7-CHLOROHEPTANOL-1 (ω-Chloro-*n*-heptyl alcohol) $CH_2.(CH_2)_5.CH_2OH$ (with Cl on the first CH_2) $C_7H_{15}OCl$ Beil. S.N. 24

M.P.	B.P.		
10–11° (1) (2)	150° at 20 mm. (1) 120° at 13.5 mm. (3)	$D_4^{15} = 0.9998$ (1)	$n_D^{25} = 1.45367$ (1)

Cryst. from lt. pet.

[For prepn. of C̄ from α,ω-heptamethylene glycol (m.p. 20.2° (3), 18° (1), b.p. 151° at 14 mm. (1), 146° at 9 mm. (3)) with conc. HCl as directed (yields: 65% (4), 46.2% (3), 43% (1)) see indic. refs.]

[C̄ with thiophenol in aq. NaOH htd. 3 hrs. gives (1) 7-hydroxy-*n*-heptyl phenyl sulfide, ndls. from pet., m.p. 49°; this prod. with $SOCl_2$ gives (1) 7-chloro-*n*-heptyl phenyl sulfide, brown oil (no consts. reported).]

[C̄ (1 mole) with Et_2NH (3–4 moles) in s.t. at 120–160° for 12–15 hrs. gives (86% yield (3)) 7-(diethylamino)heptanol-1, b.p. 132° at 9.5 mm., $D_4^{20} = 0.8681$, $n_D^{19} = 1.4561$, cf. (6); this prod. with $SOCl_2$ in C_6H_6 yields (3) (6) 7-(diethylamino)-*n*-heptyl chloride, b.p. 126° at 15 mm., $n_D^{18} = 1.4528$ (3) (corresp. B̄.HCl, m.p. 82–84° (6)).]

C̄ with morpholine gives (5) alm. quant. 7-(4-morpholinyl)heptanol-1, b.p. 155.5–155.8° at 5 mm., $D_4^{25} = 0.9783$, $n_D^{25} = 1.4747$ (corresp. *N*-phenylcarbamate, m.p. 71.0–72.0° cor.) (5). — C̄ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (4) in alm. 100% yield (as salt) *N*-(7-hydroxy-*n*-heptyl)-*N'*-phenylpiperazine, m.p. 75.5–76.5° cor. (corresp. *N*-phenylcarbamate, m.p. 96.5–97.5° cor.).

Ⓓ 7-Chloro-*n*-heptyl *N*-phenylcarbamate: ndls. from pet. or dil. alc., m.p. 76–77° (3), 76° (1).

3:0013 (1) Bennett, Mosses, *J. Chem. Soc.* **1931**, 1689–1700. (2) Bennett, Reynolds, *J. Chem. Soc.* **1935**, 139. (3) Altman, *Rec. trav. chim.* **57**, 951–952 (1938). (4) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3439–3440 (1939). (5) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3440–3441 (1939). (6) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933, *Cent.* **1934**, I 2005; *C.A.* **28**, 3081 (1934).

3:0014 10-CHLORODECANOL-1 (ω-Chloro-*n*-decyl alcohol) $CH_2.(CH_2)_8.CH_2OH$ (with Cl on the first CH_2) $C_{10}H_{21}OCl$ Beil. I - 426, I_1-(213), I_2—

M.P.	B.P.		
10–11° (1)	161–165° at 20 mm. (2) 147.5–149° at 9 mm. (3)	$D_4^{25} = 0.9630$ (1)	$n_D^{23} = 1.45796$ (1)

Cryst. from pet. eth. (1). — Almost insol. aq.; eas. sol. alc., ether, C_6H_6, pet. ether.

[For prepn. of C̄ from α,ω-decamethylene glycol [Beil. I-491, I_1-(250), I_2-(560)] (m.p. 74.5° (1)) with conc. HCl (10 vols.) on boilg. 4 hrs. (2) (3) (for improvements of this method see (1)) (yields: 65% (4), 50% (2)) see indic. refs.]

[C̄ on distn. with fused NaOH loses HCl giving two products regarded (2) as decamethylene oxide and decen-1-ol, but their structures have been questioned (3).]

C̄ with thiophenol in aq. NaOH, heated 3 hrs., yields (1) 10-hydroxy-*n*-decyl phenyl sulfide, ndls. from lt. pet., m.p. 66.5° (1); this prod. with $SOCl_2$ gives 10-chloro-*n*-decyl phenyl sulfide, cryst. from alc., m.p. 27.5° (1).

C̄ with morpholine gives (5) alm. quant. 10-(4-morpholinyl)decanol-1, m.p. 39.5–40.5°, b.p. 164.0–165.0° at 2 mm. (corresp. *N*-(α-naphthyl)carbamate, m.p. 66.5–67.5° cor. (5)). — C̄ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (5) in alm. 100%

formn. of $\bar{C}$ *from cetyl alc.* + PCl_5 *(in pres. of mesityl oxide* + Ac_2O*) (61.5% yield)* see (10). — For formn. of $\bar{C}$ from cetyl alc. with PCl_3 see (5), but note that prod. always conts. unchanged cetyl alc. (1:5945) and cetene-1 (1:7000) (12) cf. (2).]

[For prepn. of $\bar{C}$ from cetyl stearate (1:2193) with dry HCl gas (97% yield (11)), from cetyl acetate (1:2038) with dry HCl gas + $ZnCl_2$ at 180° (13) see indic. refs.]

[For formn. of $\bar{C}$ from a mixt. of K palmitate + K chloroacetate by electrolysis see (8).]

PHYSICAL BEHAVIOR OF $\bar{C}$

[For study of electrophoretic mobility of emulsions of $\bar{C}$ see (14).]

CHEMICAL BEHAVIOR OF $\bar{C}$

With Inorganic Reactants

With metals. [$\bar{C}$ with Li in dry ether under N_2 gives (100% yield (15)) $C_{16}H_{33}Li$; on carbonation of mixt. with CO_2 this is converted (51% yield (15)) to *n*-heptadecanoic acid (margaric acid) (1:0635): note, however, that $\bar{C}$ with Li in pet. eth. (b.p. 30–35°) gives (15) only 63% yield $C_{16}H_{33}Li$ and this on carbonation only 27% overall yield of margaric acid accompanied by other prods. — For analogous reacts. of $\bar{C}$ with Na see (15) (16); for react. of $\bar{C}$ with Ca in dry ether under N_2 see (15).]

$\bar{C}$ with Mg in dry ether + trace I_2 gives in 6 hrs. (96% yield (1)) $C_{16}H_{33}MgCl$.

With NH_3. [$\bar{C}$ with liq. NH_3 in alc. in s.t. at 170° for 24 hrs. gives (70% yield (17)) di-*n*-hexadecylamine, cryst. from alc., m.p. 65°, b.p. 220° at 3 mm. (17), accompanied by (24% yield (17)) *n*-hexadecylamine, m.p. 45°, b.p. 146–148° at 3 mm. ($\bar{B}$.HCl, lfts. from abs. alc., m.p. 178° (17)).]

With misc. inorg. reactants. [$\bar{C}$ over spec. prepd. Al_2O_3 at 250° loses HCl giving (94% yield (18)) of a mixt. of hexadecenes together with other prods.]

[$\bar{C}$ with KOH at 200–300° gives (19) palmitic acid (1:0650); $\bar{C}$ with alc. KSH gives (21) *n*-hexadecyl mercaptan; $\bar{C}$ with alc. K_2S gives (21) di-*n*-hexadecyl sulfide.]

[$\bar{C}$ with $Na_2SO_3.7H_2O$ (6 moles) at 190–200° for 8 hrs. under press. gives (98% yield (20)) sodium cetanesulfonate-1.]

[For study of rate of reactn. of $\bar{C}$ with KI in acetone at 50° and 60° see (3).]

With Organic Reactants

[$\bar{C}$ with alc. KOH gives (5) ethyl *n*-hexadecyl ether, f.p. 19.9° (5); $\bar{C}$ with sodium allyl oxide refluxed 30 hrs. gives (70% yield (22)) allyl *n*-hexadecyl ether, pl. from aq. alc., m.p. 25° (22).]

[$\bar{C}$ (1 mole) with 33% alc. $MeNH_2$ (1 mole) in s.t. at 140–150° for 18 hrs. gives (68% yield (17)) *N*-methyl-di-*n*-hexadecylamine, ndls. from alc., m.p. 36–37°, b.p. 269–271° at 1 mm. (17) accompanied by (15% yield (17)) *N*-methyl-*n*-hexadecylamine, b.p. 147–150° at 1 mm. ($\bar{B}$.HCl, m.p. 169–170° (17)). — $\bar{C}$ (1 mole) with Me_2NH (2 moles) in alc. in s.t. at 140° for 14 hrs. gives (82.5% yield (17)) *N*,*N*-dimethyl-*n*-hexadecylamine, b.p. 158° at 3 mm. ($\bar{B}$.HCl, lfts. from AcOEt/dioxane 5/1, m.p. 198° (17)).]

$\bar{C}$ with tertiary amines gives by addn. the corresp. quaternary ammonium salts [e.g., $\bar{C}$ with Me_3N (2 moles) in alc. in s.t. at 100–105° for 12–16 hrs. (17), or $\bar{C}$ with Me_3N (1 mole) in closed bottle at 110° for 5 hrs. (7), gives (100% yield (17)) trimethyl-*n*-hexadecyl-ammonium chloride, hygroscopic lfts. from AcOEt/alc., m.p. abt. 70° (17); for study of surface tension of aq. solns. of this salt see (7)].

$\bar{C}$ with pyridine (1 mole) in s.t. at 110° for 15 hrs. (23) or at 120° for 8 hrs. (7) gives *n*-hexadecyl-pyridinium chloride, cryst. with 1 H_2O from alc./ether or C_6H_6, m.p. 83° (23), 82° (24) [for study of surface tension (7), conductivity (24), and elec. potential (24) of aq.

solns. of this salt see indic. refs.; for cat. hydrogenation of this salt to *N*-(*n*-hexadecyl) piperidine.HCl, m.p. 180° see (23); for study of favorable effect of press. on reactn. of $\bar{C}$ with pyridine see (12)].

[For analogous reactn. of $\bar{C}$ with *N,N*-dimethyl-benzylamine (17) or with isoquinoline (23) see indic. refs.]

[For reactn. of $\bar{C}$ with α-picoline + $NaNH_2$ yielding α-(*n*-heptadecyl)pyridine, m.p 23.5°, b.p. 206° at 2.5 mm., $\bar{B}$.PkOH, m.p. 87°, or of $\bar{C}$ with γ-picoline + $NaNH_2$ yielding γ-(*n*-heptadecyl)pyridine, m.p. 33°, b.p. 207–210° at 2.5 mm., $\bar{B}$.PkOH, m.p. 115°, see (9)]

—— *n*-**Hexadecyl *p*-nitrobenzoate**: m.p 58 4° cor. (25). [Prepd. indirectly.]

—— *n*-**Hexadecyl 3,5-dinitrobenzoate**: m.p 66°. [Prepd. indirectly.]

—— *N*-(*n*-**Hexadecyl)phthalimide**: unreported.

—— *S*-(*n*-**Hexadecyl)isothiourea hydrochloride**: m p. 126–128° (26). [From $\bar{C}$ with thiourea in alc. on refluxing 3–4 days (26)]

—— *n*-**Hexadecyl mercuric chloride**: cryst. from pet. eth. or AcOEt, m.p. 114–115° (15). [Prepd. indirectly; note that m p. of mixts. of this prod. with either n-$C_{12}H_{25}HgCl$ (m p. 114–114.5°) or $C_{18}H_{37}HgCl$ (m.p 115–116°) is depressed (15).]

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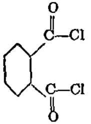
(21) Fridau, *Ann.* **83**, 16–20 (1852). (22) Davies, Heilbron, Givens, *J. Chem Soc.* **1930**, 2545. (23) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Helv. Chim Acta* **21**, 233–236 (1938) (24) Lottermoser, Frotscher, *Kolloid-Beihefte* **45**, 305–307, 316, 320, 324, 340, 343 (1937). (25) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252–2253 (1943). (26) Sprague, Johnson, *J. Am. Chem. Soc.* **59**, 1838–1839 (1937).

—— *sym.-o*-**PHTHALYL DICHLORIDE**

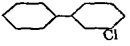


$C_8H_4O_2Cl_2$ Beil. **IX - 805**
IX_1-(363)

M.P. 16° **B.P. 276.7° at 760 mm.** D_4^{20} **= 1.4089** n_D^{20} **= 1.5692**

See 3:6900. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— **3-CHLOROBIPHENYL**



$C_{12}H_9Cl$ Beil. **V - 579**
V_1—
V_2-(483)

M.P. 16° **B.P. 284–285°**

See 3:8940. *Division B. Liquids, Section* 2, $D_4^{20} < 1.15$

formn. of C̄ from cetyl alc. + PCl_5 (in pres. of mesityl oxide + Ac_2O) (61.5% yield) see (10). — For formn. of C̄ from cetyl alc. with PCl_3 see (5), but note that prod. always conts. unchanged cetyl alc. (1:5945) and cetene-1 (1:7000) (12) cf. (2).]

[For prepn. of C̄ from cetyl stearate (1:2193) with dry HCl gas (97% yield (11)), from cetyl acetate (1:2038) with dry HCl gas + $ZnCl_2$ at 180° (13) see indic. refs.]

[For formn. of C̄ from a mixt. of K palmitate + K chloroacetate by electrolysis see (8).]

PHYSICAL BEHAVIOR OF C̄

[For study of electrophoretic mobility of emulsions of C̄ see (14).]

CHEMICAL BEHAVIOR OF C̄

With Inorganic Reactants

With metals. [C̄ with Li in dry ether under N_2 gives (100% yield (15)) $C_{16}H_{33}Li$; on carbonation of mixt. with CO_2 this is converted (51% yield (15)) to *n*-heptadecanoic acid (margaric acid) (1:0635): note, however, that C̄ with Li in pet. eth. (b.p. 30–35°) gives (15) only 63% yield $C_{16}H_{33}Li$ and this on carbonation only 27% overall yield of margaric acid accompanied by other prods. — For analogous reacts. of C̄ with Na see (15) (16); for react. of C̄ with Ca in dry ether under N_2 see (15).]

C̄ with Mg in dry ether + trace I_2 gives in 6 hrs. (96% yield (1)) $C_{16}H_{33}MgCl$.

With NH_3. [C̄ with liq. NH_3 in alc. in s.t. at 170° for 24 hrs. gives (70% yield (17)) di-*n*-hexadecylamine, cryst. from alc., m.p. 65°, b.p. 220° at 3 mm. (17), accompanied by (24% yield (17))*n*-hexadecylamine, m.p. 45°, b.p. 146–148° at 3 mm. (B̄.HCl, lfts. from abs. alc., m.p. 178° (17)).]

With misc. inorg. reactants. [C̄ over spec. prepd. Al_2O_3 at 250° loses HCl giving (94% yield (18)) of a mixt. of hexadecenes together with other prods.]

KSH gives (21)

(98% yield (20))

sodium cetanesulfonate-1.]

[For study of rate of reactn. of C̄ with KI in acetone at 50° and 60° see (3).]

With Organic Reactants

[C̄ with alc. KOH gives (5) ethyl *n*-hexadecyl ether, f.p. 19.9° (5); C̄ with sodium allyl oxide refluxed 30 hrs. gives (70% yield (22)) allyl *n*-hexadecyl ether, pl. from aq. alc., m.p. 25° (22).]

[C̄ (1 mole) with 33% alc. $MeNH_2$ (1 mole) in s.t. at 140–150° for 18 hrs. gives (68% yield (17)) *N*-methyl-di-*n*-hexadecylamine, ndls. from alc., m.p. 36–37°, b.p. 269–271° at 1 mm. (17) accompanied by (15% yield (17)) *N*-methyl-*n*-hexadecylamine, b.p. 147–150° at 1 mm. (B̄.HCl, m.p. 169–170° (17)). — C̄ (1 mole) with Me_2NH (2 moles) in alc. in s.t. at 140° for 14 hrs. gives (82.5% yield (17)) *N*,*N*-dimethyl-*n*-hexadecylamine, b.p. 158° at 3 mm. (B̄.HCl, lfts. from AcOEt/dioxane 5/1, m.p. 198° (17)).]

C̄ with tertiary amines gives by addn. the corresp. quaternary ammonium salts [e.g., C̄ with Me_3N (2 moles) in alc. in s.t. at 100–105° for 12–16 hrs. (17), or C̄ with Me_3N (1 mole) in closed bottle at 110° for 5 hrs. (7), gives (100% yield (17)) trimethyl-*n*-hexadecyl-ammonium chloride, hygroscopic lfts. from AcOEt/alc., m.p. abt. 70° (17); for study of surface tension of aq. solns. of this salt see (7)].

C̄ with pyridine (1 mole) in s.t. at 110° for 15 hrs. (23) or at 120° for 8 hrs. (7) gives *n*-hexadecyl-pyridinium chloride, cryst. with 1 H_2O from alc./ether or C_6H_6, m.p. 83° (23), 82° (24) [for study of surface tension (7), conductivity (24), and elec. potential (24) of aq.

solns. of this salt see indic. refs.; for cat. hydrogenation of this salt to N-(n-hexadecyl) piperidine.HCl, m.p. 180° see (23); for study of favorable effect of press. on reactn. of $\bar{C}$ with pyridine see (12)].

[For analogous reactn of $\bar{C}$ with N,N-dimethyl-benzylamine (17) or with isoquinoline (23) see indic. refs.]

[For reactn. of $\bar{C}$ with α-picoline + $NaNH_2$ yielding α-(n-heptadecyl)pyridine, m.p 23.5°, b.p. 206° at 2.5 mm , $\bar{B}$.PkOH, m.p. 87°, or of $\bar{C}$ with γ-picoline + $NaNH_2$ yielding γ-(n-heptadecyl)pyridine, m.p. 33°, b.p. 207–210° at 2.5 mm., $\bar{B}$.PkOH, m.p. 115°, see (9).]

—— *n*-**Hexadecyl *p*-nitrobenzoate:** m p. 58.4° cor. (25) [Prepd. indirectly.]

—— *n*-**Hexadecyl 3,5-dinitrobenzoate:** m.p. 66°. [Prepd. indirectly.]

—— *N*-(*n*-**Hexadecyl)phthalimide:** unreported.

—— *S*-(*n*-**Hexadecyl)isothiourea hydrochloride:** m.p. 126–128° (26). [From $\bar{C}$ with thiourea in alc. on refluxing 3–4 days (26)]

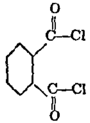
—— *n*-**Hexadecyl mercuric chloride:** cryst. from pet. eth. or AcOEt, m.p. 114–115° (15). [Prepd. indirectly; note that m.p. of mixts. of this prod. with either n-$C_{12}H_{25}HgCl$ (m.p. 114–114.5°) or $C_{18}H_{37}HgCl$ (m.p. 115–116°) is depressed (15).]

3:0015 (1) Houben, Boedler, Fischer, *Ber.* **69**, 1766–1769, 1779–1780 (1936). (2) Clark, Streight, *Trans. Roy. Soc Canada* (3) **23**, III 77–89 (1929). (3) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (4) Norris, Taylor, *J. Am. Chem. Soc.* **46**, 756 (1924) (5) Phillips, Mumford, *J. Chem Soc.* **1931**, 1732–1735. (6) Tuttscheff, *Jahresber.* **1860**, 406. (7) Hauser, Niles, *J. Phys. Chem.* **45**, 954–959 (1940). (8) Matsui, Arakawa, *Mem. Coll Sci. Kyoto Imp. Univ.* **A-15**, 189–194 (1932); *Cent.* **1932**, II 2167; *C.A* **26**, 5264 (1932). (9) Tschitschibabin, *Bull. soc. chim.* (5) **5**, 431–432 (1938). (10) Drake, Marvel, *J. Org. Chem* **2**, 394 (1937).

(11) Guyer, Bieler, Hardmeier, *Helv. Chim. Acta* **20**, 1462–1467 (1937). (12) Fawcett, Gibson, *J. Chem Soc.* **1934**, 396–400 (13) Deutsche Hydrierwerke A.G., Ger 567,014, Dec. 24, 1932; *Cent.* **1933**, I 1015; *C.A.* **27**, 1361 (1933). (14) Dickinson, *Trans Faraday Soc* **37**, 140–148 (1941). (15) Meals, *J. Org. Chem.* **9**, 211–218 (1944). (16) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 757 (1936). (17) Westphal, Jerchel, *Ber.* **73**, 1006–1011 (1940). (18) Asinger, *Ber.* **75**, 1254–1256 (1942). (19) Schrauth, Ger. 327,048, Oct. 4, 1920; *C.A.* **15**, 2009 (1921). (20) Turkiewicz, St. Pilat, *Ber.* **71**, 285 (1938).

(21) Fridau, *Ann.* **83**, 16–20 (1852). (22) Davies, Heilbron, Givens, *J. Chem Soc.* **1930**, 2545. (23) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Helv. Chim. Acta* **21**, 233–236 (1938) (24) Lottermoser, Frotscher, *Kolloid-Beihefte* **45**, 305–307, 316, 320, 324, 340, 343 (1937). (25) Armstrong, Copenhaver, *J. Am Chem. Soc.* **65**, 2252–2253 (1943). (26) Sprague, Johnson, *J. Am. Chem. Soc.* **59**, 1838–1839 (1937).

—— *sym.-o*-**PHTHALYL DICHLORIDE**

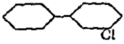


$C_8H_4O_2Cl_2$ Beil. IX - 805 IX_1-(363)

M.P. 16° **B.P. 276.7° at 760 mm.** D_4^{20} = **1.4089** n_D^{20} = **1.5692**

See 3:6900. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— **3-CHLOROBIPHENYL**



$C_{12}H_9Cl$ Beil. V - 579 V_1— V_2-(483)

M.P. 16° **B.P. 284–285°**

See 3:8940. *Division B: Liquids, Section* 2, $D_4^{20} < 1.15$.

$\bar{C}$ is insol. aq.; sol. in alc. or ether.

[For prepn. from α-chloroisovaleronitrile with conc. HCl at 100° see (1); from sodium isovalerate with aq. HOCl see (2).]

$\bar{C}$ with PCl_3 yields (1) α-chloroisovaleryl chloride (3:8144).

—— Methyl α-chloro-isovalerate: unreported.
—— Ethyl α-chloro-isovalerate: unreported.
—— α-Chloro-isovaleramide: unreported.
—— α-Chloro-isovaler-anilide: unreported.
—— α-Chloro-isovalero-p-toluidide: unreported.

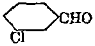
3:0050 (1) Servais, *Rec. trav. chim.* 20, 51–53 (1901). (2) Schlebusch, *Ann.* 141, 323 (1867).

—— **1,2,4-TRICHLOROBENZENE** $C_6H_3Cl_3$ **Beil. V - 204**
V_1-(112)
V_2-(156)

M.P. 17° **B.P. 213° cor.**

See 3:6420. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— **m-CHLOROBENZALDEHYDE** C_7H_5OCl **Beil. VII - 234**
VII_1-(133)



M.P. 17° **B.P. 216°** D_4^{20} = **1.2410** n_D^{20} = **1.5591**

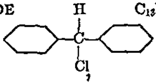
See 3:6475. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— **2,2,2-TRICHLOROETHANOL-1** $Cl_3C.CH_2OH$ $C_2H_3OCl_3$ **Beil. I - 338**
(β,β,β-Trichloroethyl alcohol) **I_1-(170)**
I_2-(337)

M.P. 17–18° **B.P. 151°**

See 3:5775. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

3:0060 BENZOHYDRYL CHLORIDE $C_{13}H_{11}Cl$ **Beil. V - 590**
(Diphenylmethyl chloride, **V_1-(278)**
diphenylcarbinyl chloride, **V_2-(500)**
diphenyl-chloromethane,
α-chlorodiphenylmethane)



M.P.		B.P.			
[20.5°	(1)]	190–191°	at 247 mm.	(12)	$D_4^{19.5}$ = 1.1398 (10) $n_D^{19.5}$ = 1.5959 (10)
18°	(2)	173°	at 19 mm.	(13) (14)	
17.6	(3)	169–170°	at 17 mm.	(10)	
17–18°	(4)	165°	at 17 mm.	(15)	
17°	(5)	167°	at 16 mm.	(4)	
13–15°	(6)	165.5°	at 15 mm.	(1)	
14.5°	(7)	161–162°	at 13 mm.	(3)	
14°	(8)	158.0–159.5°	at 12 mm.	(1)	
	(9) (24)	155–157°	at 12 mm.	(16)	
13–14°	(10)	156°	at 10 mm.	(7)	

12–14° (11)	148–150°	at 6 mm.	(6)
	146.5–147.6°	at 6 mm.	(17)
	141°	at 4 mm.	(18)
	135–145°	at 4 mm.	(8)
	119–120°	at 2.5 mm.	(19)
	113–114°	at 1.5 mm.	(5)
	115–116°	at 1 mm.	(19)
	115°	at 1 mm.	(3)

C̄ rapidly becomes turbid in contact with atmosphere and should be kept in sealed tubes (1). — C̄ on attempted distn. at ord. press. loses HCl and gives 1,1,2,2-tetraphenylethane [Beil. V-739, V_1-(371)] (20), m.p. 211°, and 1,1,2,2-tetraphenylethylene [Beil V-743, V_1-(376)] (9), m.p. 227°.

[For prepn. of C̄ from diphenylcarbinol (1:5960) with dry HCl gas alone (9) (21), or in C_6H_6 (92% yield (14)), or in C_6H_6 + $CaCl_2$ (yield: 90% (1), 85% (3)) (11) (17), with $SOCl_2$ in toluene (93.3% yield (2)), with PCl_5 in $POCl_3$ (92% yield (14)), or with $BeCl_2$ (77% yield (8)) see indic. refs.; from diphenylmethane (1:7120) with PCl_5 at 170° (together with other products) (22) or with NOCl (together with other products) (23) see indic. refs.: for formn. of C̄ from diphenylcarbinyl MgBr with ClCN (42% yield + 8% diphenylacetonitrile + 5% 1,1,2,2-tetraphenylethane) see (10); from *bis*-(diphenylcarbinyl) ether in C_6H_6 with HCl gas (77% yield) see (1); from diphenylcarbinylhydrazine with boilg. dil. HCl see (24); from diphenyldiazomethane with HCl gas in ether at −80° see (25).]

[C̄ with molecular Ag in C_6H_6 *in absence of* O_2 gives 100% yield (19) of 1,1,2,2-tetraphenylethane (see first paragraph); in pres. of pure O_2 yield drops to 2–8% and other products are formed (19); C̄ in C_6H_6 refluxed some hours with Na gives (80–90% yield (14)) (9) (21) 1,1,2,2-tetraphenylethane (see first paragraph); C̄ with Na in liq. NH_3 gives (26) 1,1,2,2-tetraphenylethane (65% yield) + diphenylmethane (1:7120) (27% yield).]

C̄ in dry ether treated with Mg + trace of I_2 immediately ppts. 1,1,2,2-tetraphenylethane whose yield may reach 95.5% (2); however, under special conditions (6) C̄ in ether with Mg + trace of I_2 gives (51–71%) corresp. RMgCl cpd.; this prod. upon treatment with CO_2 gives (yield: 84% (6), 32.5% (2)) diphenylacetic acid (1:0765), m.p. 148°; the RMgCl cpd. does *not* react (2), however, with phenyl isocyanate.

[C̄ with pure $AlCl_3$ immediately resinifies (11); however, C̄ in C_6H_6 with $AlCl_3$ gives (11) triphenyl-chloromethane (3:3410) + diphenylmethane (1:7120) with a very little triphenylmethane (1:7220).]

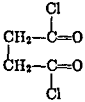
[C̄ htd. with 20% aq. Na_2SO_3 soln. for 3 hrs. at 120° gives (100% yield (28)) (27) *bis*-(diphenylmethyl) ether [Beil. VI-679, VI_1-(326)], cryst. from alc., m.p. 109° (27), 110° (17); note that this reaction probably results from intermediate diphenylcarbinol and that none of the expected sulfonate can be isolated.]

[For reactn. of C̄ with phenols + $ZnCl_2$ yielding mono-, di- or tri-alkylated phenols according to conditions see (13) (29) cf. (30); for reactn. of C̄ with thiophenols see (31); for reactn. of C̄ with excess Br.Mg.C≡C.MgBr giving (40–50% yield) 1,1,4,4-tetraphenylbutine see (32); for reactn. of C̄ with anthrone + KOH see (33).]

C̄ with aq. hydrolyzes yielding diphenylcarbinol (1:5960) or its reactn. products according to particular conditions; for extensive studies see (34) (12) (35) (18) (40) (35). — C̄ with EtOH undergoes alcoholysis yielding ethyl diphenylcarbinyl ether + HCl (for very extensive studies of this and related reactions see (1) (36) (4) (17) (37) (7) (35). — C̄ after warming with alc. may then be titrated quant. with stand. alkali using phenolphthalein (1).

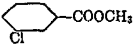
—— Diphenylcarbinyl acetate [Beil. VI-680, VI_1-(326)]: cryst. from AcOH, m.p. 40–41°. [From C̄ with KOAc in AcOH (22).]

(19) Humnicki, *Roczniki Chem.* **11**, 670-673 (1931); *Cent.* **1931**, II 3334. (20) Jusa, Riesz, *Monatsh.* **58**, 143 (1931).
(21) Günther, Haller, Köster (to I.G.), Ger. 441,326, March 1, 1927; *Cent.* **1927**, I 2358. (22) Farbwerke Meister Lucius & Brüning, Ger. 360,401, Oct. 3, 1922; *Cent.* **1923**, II 479. (23) Chem. Fabrik. von Heyden, Ger. 365,212, Dec. 11, 1922; *Cent.* **1923**, II 251. (24) Kaufmann, *Arch. Pharm.* **265**, 235-236 (1927).

—— SUCCINYL (DI)CHLORIDE  $C_4H_4O_2Cl_2$ **Beil. II - 613**
II_1-(264)
II_2-(553)

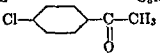
M.P. 20° **B.P. 193° at 760 mm.** D_4^{20} **= 1.3748** n_D^{20} **= 1.4683**

See 3:6200. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— METHYL *m*-CHLOROBENZOATE  $C_8H_7O_2Cl$ **Beil. IX-338**
IX_1—

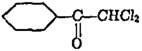
M.P. 20-21° **B.P. 231° at 763.5 mm.**

See 3:6670. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— *p*-CHLOROACETOPHENONE C_8H_7OCl **Beil. VII - 281**
VII_1-(151)


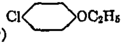
M.P. 20-21° **B.P. 232°** D_{-}^{20} **= 1.188**

See 3:6735. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

—— *ω,ω*-DICHLOROACETOPHENONE $C_8H_6OCl_2$ **Beil. VII - 282**
VII_1-(152)


M.P. 20° **B.P. 247-248°**

See 3:6835. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

3:0090 *p*-CHLOROPHENETOLE  C_8H_9OCl **Beil. VI - 187**
(*p*-Chlorophenyl ethyl ether) **VI_1—**
VI_2-(176)

M.P. 21° (1) **B.P. 211.6° cor. (3)** $D_{20.2}^{20.2}$ **= 1.12310 (2)** n_D^{19} **= 1.5227 (5)**
20.9° (2) **210-212° (1)(4)**
20° (3)

Colorless oil, volatile with steam (6).

[For prepn. from *p*-chlorophenol (3:0475) + C_2H_5I in presence of KOH see (1), in presence of K_2CO_3 + acetone (74% yield) see (4).]

$\bar{C}$ grad. added to 2 pts. conc. HNO_3 ($D = 1.485$) with cooling, then poured into aq., gives (6) 4-chloro-2-nitrophenetole [Beil VI-238], pale yel. ndls. from alc., m p. 61° (6). [The mother liquor contains some 4-chloro-2,6-dinitrophenol [Beil. VI-260], m.p. 80° (6).]

C̄ htd. at 100° with abt. 30 pts. of a soln. of const.-boilg. HBr (1 vol.) in AcOH (2 vols.) for 2 hrs. gave (4) 85% yield of p-chlorophenol (3:0475).

Ⓓ **5-Chloro-2-ethoxybenzenesulfonamide:** cryst. from dil. alc., m.p. 134–134.5° u.c. (7). [From C̄ by treat. with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with $(NH_4)_2CO_3$ (71% yield (7))]. [Note that this prod. depresses the m.p of the corresponding deriv. (m.p. 132–133° u.c.) from o-chlorophenetole (3·8735) (7).]

3:0090 (1) Beilstein, Kurbatow, *Ann.* **176**, 31 (1875). (2) Swarts, *J. chim. phys.* **20**, 76 (1923). (3) Peratoner, Ortoleva, *Gazz. chim. ital.* **28**, I 226 (1898). (4) Borosel, *J. Am. Chem. Soc.* **53**, 1408–1409 (1931). (5) Cotton, Mouton, *Ann. chim.* (8) **28**, 216 (1913). (6) Reverdin, During, *Ber.* **32**, 153 (1899). (7) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603–604 (1940).

3:0095 1-CHLORO-OCTADECANE $CH_3(CH_2)_{16}.CH_2Cl$ $C_{18}H_{37}Cl$ **Beil. S.N. 10**
(n-Octadecyl chloride;
stearyl chloride)

M.P. 21° (1) **B.P. 180–190°** at 12 mm. (1) (2)
18° (2)

Care must be taken to avoid confusion of C̄ with the acid chloride of stearic acid which is often designated as stearoyl chloride (3·9960).

[For prepn. of C̄ from octadecanol-1 (stearyl alc.) (1:5953) with excess PCl_5 on htg. (no statement of yields) (1) (10) or with PCl_5 in $SOCl_2$ (100% yield (10)) see indic. refs.]

[For study of heat of adsorption of C̄ on steel and its bearing on lubrication see (1); for study of electrophoretic mobility of emulsions of C̄ see (3).]

C̄ with Mg in dry ether yields (4) n-$C_{18}H_{37}MgCl$ [this prod. with cyclopentanone (1:5446) gives (4) a tertiary alc. which on dehydration with $KHSO_4$ yields (4) n-octadecylcyclopentene, b.p. 173–174° at 3 mm., m.p. 19°, $D_4^{20} = 0.8462$; similarly $C_{18}H_{37}MgCl$ with cyclohexanone (1:5465) gives (4) a tertiary alc. which with $KHSO_4$ loses aq. giving (4) n-octadecylcyclohexene, b.p. 179–180° at 3 mm., m.p. 20°, $D_4^{20} = 0.8458$].

[C̄ with C_6H_6 + $AlCl_3$ undergoes Friedel-Crafts reactn. yielding (4) n-(?)-octadecylbenzene [Beil. V-473, V_1-(361)], m.p. 25–26°, b.p. 180–181° at 3 mm., $D_4^{20} = 0.8566$, $n_D^{20} = 1.4826$.]

C̄ (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (5) the corresp. quaternary salt, N-(n-octadecyl)pyridinium chloride, cryst. from alc./ether or C_6H_6 as monohydrate, m.p. 82° (5), 86° (6); for study of conductivity and electric potential of latter see (6).

—— **n-Octadecyl p-nitrobenzoate:** m.p. 64.3° cor. (7). [Prepd. indirectly.]
—— **n-Octadecyl 3,5-dinitrobenzoate:** unreported.
—— **N-(n-Octadecyl)phthalimide:** unreported.
—— **S-(n-Octadecyl)isothiourea:** m.p. 83–85° (8). [Prepd. indirectly.]
—— **n-Octadecyl mercuric chloride:** m.p. 115–116° (9). [Prepd. indirectly: note that m.p. of this prod. either with $C_{16}H_{33}HgCl$ (m.p. 114–115°) or with $C_{18}H_{37}HgBr$ (m.p. 110–111°) is depressed (9).]

3:0095 (1) Frewing, *Proc. Roy. Soc.* (*London*) **A-182**, 270–286 (1944). (2) Meyer, Streuli, *Helv. Chim. Acta* **20**, 1179–1183 (1937). (3) Dickinson, *Trans. Faraday Soc.* **37**, 140–148 (1941). (4) Suida, Gemassner, *Ber.* **72**, 1168–1173 (1939). (5) Karrer, Kahnt, Epstein, Jaffe, Ishii, *Helv. Chim. Acta* **21**, 233–234 (1938). (6) Lottermoser, Frotscher, *Kolloid-Beihefte* **45**, 305–306, 320–321, 325, 341 (1937). (7) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252–2253 (1943). (8) Snell, Weissberger, *J. Am. Chem. Soc.* **61**, 453 (1939). (9) Meals, *J. Org. Chem.* **9**, 213–217 (1944). (10) Davies, Heilbron, Owens, *J. Chem. Soc.* **1930**, 2546.

—— *n*-OCTADECANOYL CHLORIDE $C_{18}H_{35}OCl$ Beil. II - 384
(Stearoyl chloride) $CH_3.(CH_2)_{16}—C(=O)Cl$ II_1-(176)
II_2-(360)

M.P. 23–24° **B.P. 215° at 15 mm.**

See 3:9960. *Division C: Liquids with b.p. reported only at reduced pressure.*

3:0100 1-CHLOROHEPTADECANE $CH_3.(CH_2)_{15}.CH_2Cl$ $C_{17}H_{35}Cl$ **Beil. I —**
(*n*-Heptadecyl chloride) **I_1-(69)**
I_2—

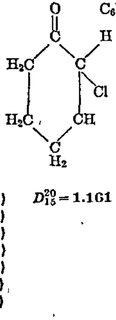
M.P. 24° (1) **B.P. 192–195° at 10 mm. (1)**

[For prepn. of C̄ from *N*-benzoylheptadecylamine (*N*-(*n*-heptadecyl)benzamide) with PCl_5 on distn. (50% yield) see (1); from silver stearate (or other stearates of metals of 1st, 2nd, or 3rd group) with Cl_2 see (2).]

—— *n*-Heptadecyl *p*-nitrobenzoate: m.p. 53.8° cor. (3). [Prepd. indirectly.]
—— *n*-Heptadecyl 3,5-dinitrobenzoate: unreported.
—— *N*-(*n*-Heptadecyl)phthalimide: unreported.
—— *S*-(*n*-Heptadecyl)isothiourea picrate: unreported.
—— *n*-Heptadecyl mercuric chloride: unreported.

3:0100 (1) von Braun, Sobecki, *Ber.* **44**, 1473 (1911). (2) C. Hunsdiecker, H. Hunsdiecker, E. Vogt, U.S. 2,176,181, Oct. 17, 1939; *C.A.* **34**, 1686 (1940): Brit. 456,565, Dec. 10, 1936; *Cent.* **1937**, I 2258; *C.A.*, **31**, 2233 (1937): French 803,941, Oct. 12, 1936; *Cent.* **1937**, I 2258; [*C.A.* **31**, 2616 (1937)]. (3) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252–2253 (1943).

3:0120 2-CHLOROCYCLOHEXANONE-1 C_6H_9OCl **Beil. VII - 10**
VII_1-(8)



M.P.		B.P.			
24°	(1)	90–91° at 14–15 mm.	(19)	$D^{20}_{15} = 1.161$ (6)	$n^{20}_D = 1.4825$ (6)
23–24°	(2)	88–90° at 16 mm.	(5)		
23.2° cor.	(19)	82–85° at 14 mm.	(8)		
23° (3) (4) (5)		82° at 13 mm.	(4)		
22–23° (6) (7)		82–83° at 10 mm.	(3)		
		80.5° at 11 mm.	(5)		
		79° at 7 mm.	(6)		

C̄ has very disagreeable physiological effects; breathing of its ether solutions or exposure of skin to its vapor produces violent illness and temporary complete blindness; also produces an eczema on the hands (although sensitivity of individuals varies) (9). — C̄ dec. slightly on distn. even in vacuo (10).

[For prepn. from cyclohexanone (1:5465) with Cl_2 + H_2O (61–66% yield (19)), by actn. of Cl_2 + $CaCO_3$ + H_2O (HOCl) (50–60% yield (7) (8)) see (7) (8) (10) (3) (4); by direct

actn. of Cl_2 in AcOH (100% yield (8)) see (8); via N-chlorourea (80% yield (5)) or electrochem. chlorination in HCl (18); for prepn. from cyclohexanol (1.6415) by actn. of Cl_2 + $CaCO_3$ + H_2O (HOCl) (50–60% yield (6) (9)) (1) see these; for prepn. (57% yield (5)) from 2-chlorocyclohexanol-1 (3:0175) by oxidn. with $K_2Cr_2O_7$ + H_2SO_4 + AcOH see (5).]

C̄ with alc. KOH (11) yields (by ring contraction) cyclopentanecarboxylic acid [Beil. IX-6] or its ethyl ester [Beil. IX_1-(4)] — C̄ with dil. alk. (3) or boilg. conc. K_2CO_3 soln. (3) (12) or shaking with 40% K_2CO_3 (50% yield (13)) gives corresp. alc., viz , cyclohexanol-2-one-1 or adipoin [Beil. $VIII_1$-(504)], cryst. from alc., m.p. 113° (3) (14) (after fusion remelts at 90° (14), 98° (13), 92–92.5° (12). [Adipoin gives oxime, m.p. 102–103° (13); p-nitrophenylhydrazone, m.p. 146° dec. (14); semicarbazone, m p. 238° (13); benzoate, m p. 122–123° (13).]

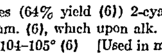
C̄ with NaCN (2 moles) in alc gives (64% yield (6)) 2-cyanocyclohexanone-1, b.p. 140–141° at 15 mm. or 129–131° at 7 mm. (6), which upon alk. hydrolysis gives (84.7% yield (6)) n-pimelic acid (1.0456), m.p. 104–105° (6) [Used in mfg. of pimelic acid (15).]

C̄ with ter-butyl-, cyclohexyl-, or isopropyl MgCl is reduced to cis-2-chlorocyclohexanol (3:9374). [C̄ with other R.Mg.X cpds. leads to 5-membered ring cpds. which cannot be considered here]

[C̄ with diazomethane gives (7) (100% yield (17)) α-chlorocycloheptanone.]

3:0120 (1) Vavon, Mitchovitch, *Bull. soc chim.* (4) **45**, 965 Note (a) (1929). (2) Favorskii, [illegible] 3) Bouveault, Chereau, [illegible] (1909) (5) Detoeuf, [illegible] 291–1295 (1933). (7) [illegible] *J. Am. Chem. Soc.* **56**, [illegible] Kendall, *J. Am. Chem. Soc.* **42**, 2618 (1920). [illegible] (1[illegible] (1[illegible] Ja[illegible] 224–227 (1935). (17) Giratis, Bullock, *J Am. Chem. Soc.* **59**, 945 (1937). (18) Szper, *Bull. soc. chim.* (4) **51**, 656 (1932) (19) Newman, Farbman, Hipsher, *Org. Syntheses*, **25**, 22–24 (1945).

—— 4-METHOXYBENZOYL CHLORIDE $C_8H_7O_2Cl$ Beil. X - 163
X_1-(77)



M.P. 24° B.P. 262–263° D_4^{20} = 1.2609 n_D^{20} = 1.5802

See 3:6890 *Division B: Liquids, Section* 1, D_4^{20} > 1.15.

3:0138 *ter*-BUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. S.N. 160
$Cl_3C.CO.O.C_4H_9$

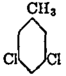
M.P. 25.5° (1) B.P. 37° at 1 mm. (1) D_4^{25} = 1.2363 (1) n_D^{25} = 1.4398 (1)

Cryst. from pentane or MeOH at 0° (1).

[For prepn. of C̄ from trichloroacetyl chloride (3:5420) with ter-butyl alc. (1:6140) in pyridine in cold (95% yield (1)), or from trichloroacetic acid (3.1150) with isobutylene at 60° (80% yield (1)) see indiv. refs.]

3:0138 (1) Scovill, Burk, Lankelma, *J. Am. Chem. Soc.* **66**, 1039 (1944).

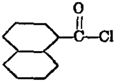
— 3,5-DICHLOROTOLUENE $C_7H_6Cl_2$ Beil. V -296
V_1—
V_2—



M.P. 26° B.P. 201–202° cor. at 760 mm.

See 3:6310. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

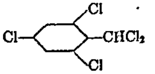
— α-NAPHTHOYL CHLORIDE $C_{11}H_7OCl$ Beil. IX - 648
IX_1-(275)



M.P. 26° B.P. 297.5°

See 3:6930. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

3:0142 2,4,6-TRICHLOROBENZAL (DI)CHLORIDE $C_7H_3Cl_5$ Beil. S.N. 466
(2,4,6-Trichlorobenzylidene (di)chloride)



M.P. 27° (1) B.P. 158° at 15 mm. (1)

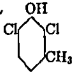
Cryst. from MeOH

[For prepn. of C̄ from 2,4,6-trichlorotoluene (3:0380) with Cl_2 at 200° (82% yield) see (1).]

C̄ on hydrolysis with fumg. H_2SO_4 gives (94% yield (1)) 2,4,6-trichlorobenzaldehyde (3:1200).

3:0142 (1) Lock, *Ber.* 66, 1532 (1933).

3:0150 2,6-DICHLORO-3-METHYLPHENOL $C_7H_6OCl_2$ Beil. VI —
(2,6-Dichloro-*m*-cresol) VI_1—
VI_2-(356)



M.P. 27° (1)	B.P. 240.5–242.5°		(1)
	239.5–240.5°	at 745 mm.	(2)
	80–85°	at 4 mm.	(2)

[For prepn. of C̄ from 4-amino-2,6-dichloro-3-methylphenol (1) via diazotization and treatment with alk. $SnCl_2$ (very poor yield) see (1); from 3-methylphenol-2,6-disulfonic acid (1) or from 3-methylphenolsulfonic acid-6 in nitrobenzene (2) with Cl_2 see indic. refs.; from 2-chloro-3-methylphenol (3:1055) or from 6-chloro-3-methylphenol (3:0700) in cold $CHCl_3$ with 1 mole Cl_2 see (1); from *m*-cresol (1:1730) in $CHCl_3$ at 0° with Cl_2 (other products are also formed) see (1).]

C̄ in $CHCl_3$ with 1 mole Cl_2 gives alm. quant. yield (1) 2,4,6-trichloro-*m*-cresol (3:0618), m.p. 46° (1).

C̄ in $CHCl_3$ with 1 mole Br_2 yields (2) 2,6-dichloro-4-bromo-3-methylphenol, m.p. 64–65° (2).

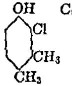
Ⓓ 2,6-Dichloro-3-methylphenyl benzoate: clusters of small prismatic pl. from alc., m.p. 90.5° (1). [From C̄ with benzoyl chloride in pyridine (1).]

Ⓓ 2,6-Dichloro-3-methylphenyl benzenesulfonate: thin lustrous pl. from alc., m.p. 70° (1). [From C̄ with benzenesulfonyl chloride in pyridine (1).] [Note proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,4-dichloro-3-methylphenol (3:1205).]

Ⓓ 2,6-Dichloro-3-methylphenyl *p*-toluenesulfonate: small pr. from alc., m.p. 92–92.5° (1). [From C̄ with *p*-toluenesulfonyl chloride in pyridine (1).]

3:0150 (1) Huston, Chen, *J. Am. Chem. Soc.* **55**, 4217–4218 (1933). (2) Huston, Neely, *J. Am. Chem. Soc.* **57**, 2178 (1935).

3:0158 2-CHLORO-3,4-DIMETHYLPHENOL C_8H_9OCl Beil. SN. 529
(3-Chloro-*o*-4-xylenol)



M.P. 27° (1)

Cryst. from lt. pet.

[For prepn. of C̄ from 2-amino-3,4-dimethylphenol (3-amino-*o*-4-xylenol) (1) via diazotization and use of Cu_2Cl_2 reaction (yield not stated) see (1).]

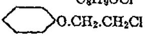
The nitration of C̄ has not been reported, and neither of the two possible mononitro-derivs. nor the corresp. dinitro-deriv. is known.

—— 2-Chloro-3,4-dimethylphenyl acetate: unreported.

Ⓓ 2-Chloro-3,4-dimethylphenyl benzoate: m.p. 87° (1).

3:0158 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.*, **1928**, 2531.

3:0165 β-PHENOXYETHYL CHLORIDE C_8H_9OCl Beil. VI - 142, VI₁-(81), VI₂-(144)
(β-Chloroethyl phenyl ether, ω-chlorophenetole)



M.P. 25° (1) (2)	**B.P.** 217–220°	at 760 mm.	(1) (4)
28° (5) (4) (3)	221°	at 754 mm.	(2)
	220°		(6)
	122.3°	at 26 mm.	(7)
	103–104°	at 12 mm.	(8)
	100–102°	at 12 mm.	(5)

Insol. aq., very eas. sol. alc., ether, C_6H_6, lgr.

[For prepn. from β-phenoxyethyl alcohol (1.6518) + $SOCl_2$ + pyridine (88% yield (7)) see (7) (1); from sodium phenolate + ethylene dichloride (3:5130) (poor yield) see (5) (3); from ethylene chlorobromide see (6) (1)].

C̄ + $AlCl_3$ + phthalic anhydride in CS_2 yields (9) *o*-[4(?)-(β-chloroethyl)-benzoyl]-benzoic ac., cryst. from C_6H_6, m.p. 145° (9).

Ⓓ *N*-(β-Phenoxyethyl)tetrachlorophthalimide: rods from acetone, m.p. 155–156° (10) [From C̄ with K tetrachlorophthalimide (10).]

3:0165 (1) Jones, *J. Chem. Soc.* **1936**, 1861. (2) Henry, *Compt. rend.* **96**, 1233 (1883). (3) Clemo, Perkin, *J. Chem. Soc.* **121**, 644–645 (1922). (4) Butler, Renfrew, Cretcher, Souther, *J. Am. Chem. Soc.* **59**, 229 (1937). (5) Wohl, Berthold, *Ber.* **43**, 2179 (1910). (6) Bentley, Haworth, Perkin, *J. Chem. Soc.* **69**, 165 (1896). (7) Kirner, *J. Am. Chem. Soc.* **48**, 2748 (1926). (8) Földi, *Ber.* **53**, 1845 (1920). (9) Bruson, Eastes, *J. Am. Chem. Soc.* **60**, 2504 (1938). (10) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934).

3:0170 9-CHLORONONANOL-1 $CH_2.(CH_2)_7.CH_2OH$ (with Cl on the first CH_2) $C_9H_{19}OCl$ Beil. S.N. 24
(ω-Chloro-*n*-nonyl alcohol)

M.P. 28° (1) **B.P. 140–145° at 20 mm. (1)**
146.5° at 14 mm. (2)

Cryst. from lt. pet.

[For prepn. of C̄ from α,ω-nonamethylene glycol [Beil. I_2-(558)] (m.p. 46° (1)) with conc. HCl as directed (yields: 90% (1), 86% (2), 65% (3)) see indic. refs.]

C̄ with thiophenol in aq. NaOH htd. 3 hrs. gives (1) 9-hydroxy-*n*-nonyl phenyl sulfide, cryst. from lt. pet., m.p. 60°. [This prod. with $SOCl_2$ gives (1) 9-chloro-*n*-nonyl phenyl sulfide, cryst. from aq. alc. at low temp., m.p. 5° (1).]

[C̄ (1 mole) with Et_2NH (3–4 moles) in s.t. at 120–160° for 12–15 hrs. gives (90% yield (2)) 9-(diethylamino)nonanol-1, b.p. 161.5° at 12 mm., $D_4^{15.4} = 0.8635$, $n_D^{19} = 1.4574$ (2), cf. (5); this prod. with $SOCl_2$ in C_6H_6 gives (2) (5) 9-(diethylamino)-*n*-nonyl chloride, b.p. 145° at 10 mm., $n_D^{17.5} = 1.4535$ (2) (corresp. B̄.HCl, m.p. 85–86° (5)).]

C̄ with morpholine gives (4) alm. quant. 9-(4-morpholinyl)nonanol-1, m.p. 31°, b.p. 173.0–173.5° at 5 mm. (corresp. *N*-(α-naphthyl)carbamate, m.p. 54.0–56.0° cor.). — C̄ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) *N*-(9-hydroxy-*n*-nonyl)-*N'*-phenylpiperazine, m.p. 80.0–80.5° cor. (corresp. *N*-phenylcarbamate, m.p. 94.0–95.0° cor.).

Ⓓ **9-Chloro-*n*-nonyl *N*-phenylcarbamate:** cryst. from dil. alc., m.p. 70.0–70.5° (3), 67° (1) (2).

Ⓓ **9-Chloro-*n*-nonyl *N*-(*m*-nitrophenyl)carbamate:** m.p. 57° (2).

3:0170 (1) Bennett, Mosses, *J. Chem. Soc.* **1931**, 1697–1701. (2) Altman, *Rec. trav. chim.* **57**, 951–952 (1938). (3) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3439–3440 (1939). (4) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3440–3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933; *Cent.* **1934**, I 2005; *C.A.* **28**, 3081 (1934).

3:0172 12-CHLORODODECANOL-1 $C_{12}H_{25}OCl$ Beil. S.N. 24
(ω-Chloro-*n*-dodecyl alcohol; ω-chlorolauryl alcohol) $CH_2.(CH_2)_{10}.CH_2OH$ (with Cl on the first CH_2)

M.P. 28° (1) **B.P. 134° at 1 mm. (1)**

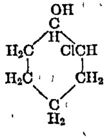
Colorless cryst. from lt. pet.

[For prepn. of C̄ from α,ω-dodecamethylene glycol [Beil. I_2-(562)] (m.p. 83.5–84.5° (1)) with conc. HCl on htg. as directed (50% yield crude prod.) see (1).]

Ⓓ **12-Chlorododecyl *N*-phenylcarbamate:** ndls. from pet., m.p. 66° (1).

3:0172 (1) Bennett, Gudgeon, *J. Chem. Soc.* **1938**, 1679–1681.

3:0175 *trans*-2-CHLOROCYCLOHEXANOL-1 $C_6H_{11}OCl$ Beil. VI - 7
(*trans*-Cyclohexene chlorohydrin) VI_1—
VI_2-(12)



M.P.	B.P.				
29° (1) (2)	104–106°	at 45 mm. (4)	$D^{35}_{-} = 1.1233$ (3)		$n^{35}_D = 1.4832$ (3)
27° (3)	93°	at 26 mm. (3)			
	88–90°	at 20 mm. (4)	$D^{16}_{-} = 1.146$ (1)		$n^{16}_D = 1.4850$ (1)
	85–86°	at 17 mm. (26)			
	84–85°	at 16 mm. (2) (7)			
	87°	at 15 mm. (1)			
	92°	at 10 mm. (5)			

[*See also cis-2-chlorocyclohexanol*-1 (3:9374).]

Both the two theoretically possible geometrical stereoisomers of 2-chlorocyclohexanol-1 are known. The single form obtained from cyclohexene (tetrahydrobenzene) by addn. of HOCl or from cyclohexene oxide by addn. of HCl is now regarded (3) as the *trans* isomer C̄. The *cis* form (3:9374) is obtd. by other methods.

Colorless pr. from mixt. of C_6H_6 + lgr. at low temp.; C̄ has characteristic odor, is vol. with steam.

[For prepn. of C̄ from cyclohexene (tetrahydrobenzene) (1·8070) with HOCl (yields: 70–73% (4), 70% (5)) (6) (7) (8) or with *N*-chlorourea (yield: 74% (26), 54% (9)) see indic. refs.; from cyclohexene oxide (see below) with conc. HCl or with $ZnCl_2$ in dry ether see (3); for probable formn. of C̄ from cyclohexene (1:8070) with EtOCl (3:7022) see (10); for formn. of a mixt. of both stereoisomeric 2-chlorocyclohexanols contg. 27–28% C̄ + 72–73% *cis*-isomer from 2-chlorocyclohexanone (3:0120) by reductn. with isopropyl MgCl, *ter*-butyl MgX, or cyclohexyl MgX see (3); for formn. of a mixt. (b.p. 78–80° at 12 mm.) of both isomers by hydrolysis of 2-chlorocyclohexanyl acetate see (11).]

C̄ with aq. NaOH at room temp. gives (yields. 70–73% (12), 70–75% (5), 80% (9), 55% (13)) cyclohexene oxide (1,2-epoxycyclohexane) [Beil. XVII-21], b.p. 131.5° at 760 mm. [Note that reactn. of C̄ with alk. is 300 times as fast as that of the *cis* isomer (3:9374) (use in detn. of proportion of C̄ in mixts. of isomers), that the latter with alk. gives no epoxy cpd. but instead cyclohexanone, and finally that C̄ can be separated from its isomer by conversion to cyclohexene oxide from which the remaining *cis* isomer can be sepd. by distn. (3).]

C̄ with alk. or with alc. KCl is *not* converted to *cis* isomer (3) but C̄ on protracted htg. with HCl rearr. to a small extent to the *cis* isomer.

[For use of C̄ as seed disinfectant see (15).]

The halogen atom of C̄ is fairly reactive, but its replacement often involves rearr. of the cyclohexyl ring to a cyclopentyl ring.

[C̄ on boilg. with dil. alc. slowly gives (1) *trans*-cyclohexanediol-1,2 [Beil. VI-740] with cyclopentylformaldehyde (formylcyclopentane), the latter increasing in pres. of dil. H_2SO_4 or of $CaCl_2$ (1).]

[C̄ with NaOMe in MeOH yields (14) *cis*-2-methoxycyclohexanol-1 [Beil. VI-740], b.p. 181.5° at 760 mm., $D^{20}_{-} = 1.015$, $n^{20}_D = 1.4605$ (14); C̄ with NaOEt in EtOH (14) (or C̄ in EtOH treated with Na in attempted reductn. (16) gives (87% yield (16)) *cis*-2-ethoxycyclohexanol-1 [Beil. VI-740], b.p. 187° at 760 mm., $D^{20}_{-} = 0.982$, $n^{20}_D = 1.4563$ (14); C̄ with sodium *n*-propylate yields (14) 2-*n*-propoxycyclohexanol, b.p. 205° at 760 mm., $D^{20}_{-} = 0.970$, $n^{20}_D = 1.4580$ (14); C̄ with sodium cyclohexanolate yields (14) 2-cyclohexanoxycyclohexanol, m.p. 50° (14).]

[C̄ with $C_6H_5.CH_2MgCl$ gives (54% yield (17)) benzyl-cyclopentyl-carbinol, b.p. 166–169° at 20 mm., m.p. 30° (3,5-dinitrobenzoate, m.p. 100.5–101.5° (17)). — C̄ with excess MeMgI gives (50% yield (13)) mixt. of both *cis* and *trans* 2-methylcyclohexanols (1:6420). — C̄ with cyclohexyl MgCl (cf. 3:8040) yields (18) cyclohexyl-cyclopentyl-carbinol, m.p.

34° (*p*-nitrobenzoate, m.p. 49–50°, 3,5-dinitrobenzoate, m.p. 102°, acid phthalate, m.p. 92–93°, *N*-phenylcarbamate, m.p. 122° (18)).]

[$\bar{C}$ with conc. aq. NH_4OH shaken for 24 hrs. (19) or $\bar{C}$ with NH_3 in alc. htd. in s.t. for 1 hr. (6) gives (yields: 71% (19), 61% (6)) *cis*-2-aminocyclohexanol [Beil. XIII-348], m.p. 65° (19) (6), b.p. 110° at 24 mm. (19). — $\bar{C}$ with diethylamine (2 moles) htd. in s.t. at 150° for several hrs. (20) (or similarly with BuOH as solvent (21)) yields 2-(diethylamino)-cyclohexanol, b.p. 225° at 740 mm. (21), 224° at 730 mm. (20), D^{25}_{25} = 0.9280 (21), n^{24}_{D} = 1.4659 (21) (hydrochloride, m.p. 170.5–171.5° (21)). — $\bar{C}$ with 5 pts. piperazine hydrate htd. 3 hrs. at 140° gives (22) both *N,N'-bis*-(2-hydroxycyclohexyl)piperazine, m.p. 205–206° (22), and *N*-(2-hydroxycyclohexyl)piperazine, m.p. 67–68° (22) (the latter separable by treatment of mixt. with CS_2 pptg. its dithiocarbamate).]

[$\bar{C}$ also reacts as a secondary alcohol: e.g., $\bar{C}$ with PCl_5 yields (14) 1,2-dichlorocyclohexane [Beil. V-22, V_1-(8)], b.p. 187–189°, $\bar{C}$ with PBr_5 yields (14) 1-bromo-2-chlorocyclohexane, b.p. 94° at 17 mm., D^{20}_{-} = 1.514, n^{20}_{D} = 1.5481 (14).]

$\bar{C}$ on oxidn. with $K_2Cr_2O_7/H_2SO_4$/AcOH gives (57% yield (9)) 2-chlorocyclohexanone (3:0120).

(Note: the following derivatives are listed as *cis* on the assumption of inversion during formation.)

—— *cis*(?) **2-Chlorocyclohexanyl acetate:** oil with odor like EtOAc, b.p. 95–96° at 11 mm. (23), 99–101° at 13 mm. (24), D^{25}_{25} = 1.1182 (23), n^{25}_{D} = 1.46195 (23). [From $\bar{C}$ with AcCl at 10–20° (23) or in C_6H_6 (espec. in pres. of K_2CO_3 or $BaCO_3$) (70% yield (24)), or from cyclohexene (1:8070) with Ac_2O or with Ac_2O + SO_2Cl_2 in $CHCl_3$ (11).] [This ester with MeOH + dry HCl gas yields $\bar{C}$ (11). Cf. (25).]

—— *cis*(?) **2-Chlorocyclohexanyl benzoate:** lfts. from dil. alc., m.p. 120–121° (24). [From $\bar{C}$ with BzCl htd. 10 hrs. (70% yield) (24).]

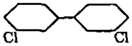
—— *cis*(?) **2-Chlorocyclohexanyl *p*-nitrobenzoate:** cryst. from dil. alc., m.p. 240° dec. (24). [From $\bar{C}$ with *p*-nitrobenzoyl chloride in dry ether or C_6H_6 + Na_2CO_3 refluxed 5 hrs. (70% yield) (24).]

—— *cis*(?) **2-Chlorocyclohexanyl *N*-phenylcarbamate:** m.p. 97–98° (2), 94–96° (17). [From $\bar{C}$ with phenyl isocyanate in lt. pet. (17).]

—— *cis*(?) **2-Chlorocyclohexanyl *N*-(α-naphthyl)carbamate:** m.p. 165° (3). [From $\bar{C}$ with α-naphthyl isocyanate at 100° for 4 hrs. (3).]

3:0175 (1) Godchot, Mousseron, Granger, *Compt. rend.* **200**, 748–749 (1933). (2) Godchot, *Compt. rend.* [illegible]
Johnstone, *Or*[illegible]
(1932); **5**, 31-[illegible]
(1926). (6) [illegible]
Soc. **73**, 948 [illegible]
1938, II 952. [illegible]
Dirsch, *Ber.* **58**, 574 (1925).
(11) Friese, Dj'iang, *Ber.* **71**, 667–670 (1938). (12) Osterberg, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 185–186 (1941); Coll. [illegible] dchot, Bedos, *Bull. soc. chim.* (4) **37**, [illegible] **205**, 327–328 (1937). (15) Consolid[illegible] 3835.
(16) Kötz, Busch, *J. prakt. Chem.* (2) **119**, 36 (1928). (17) Cook, Hewitt, Lawrence, *J. Chem. Soc.* **1936**, 74–75. (18) Vavon, Mitchovitch, *Compt. rend.* **186**, 703–705 (1928). (19) Wilson, Read, *J. Chem. Soc.* **1935**, 1272. (20) Osterberg, Kendall, *J. Am. Chem. Soc.* **43**, 1370–1371 (1921).
(21) Heckel, Adams, *J. Am. Chem. Soc.* **49**, 1305–1306 (1927). (22) Mousseron, *Bull. soc. chim.* (4) **51**, 790–793 (1932). (23) Bedos, *Compt. rend.* **183**, 562–565 (1926); *Cent.* **1926**, II 2795. (24) Kötz, Merkel, *J. prakt. Chem.* (2) **113**, 64–65 (1926). (25) Winstein, Buckles, *J. Am. Chem. Soc.* **65**, 616 (1943). (26) Newman, Vander Werf, *J. Am. Chem. Soc.* **67**, 235 (1945).

3:0180 3,3'-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ Beil. V - 579
V_1-(272)
V_2-(484)



M.P. 29° (1) (6) B.P. 322–324° (2)
23° (2) (3) 320–326° (4)
320–330° (1)
298° (6)

White ndls. from dil. alc.; eas. sol. alc., ether, C_6H_6.

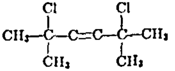
[For prepn. of C̄ from *m*-chloroiodobenzene [Beil. V-220] by htg. with Cu powd. under various conditions (yield: 95% (5), 67% (2), 61% (1)) see indic refs.; from 3,3'-dinitrobiphenyl with $SOCl_2$ *in s.t. at 200–210° for 10 hrs. see (4), from 3,3'-dichloro-4,4'-diamino*biphenyl (3,3'-diaminobenzidine) [Beil XIII-234, $XIII_1$-(67)] via tetrazotization and htg. with alc. see (6); from 3,3'-dichloro-2,4'-diaminobiphenyl via tetrazotization and treatment with H_3PO_2 see (3).]

C̄ on tetranitration, e.g., with mixt. of 5 pts. abs. HNO_3 + 20 pts conc. H_2SO_4 for 2 hrs. at 100° (5), yields (5) (7) 3,3'-dichloro-4,6,4',6'-tetranitrobiphenyl [Beil. V_1-(274)], m p. 191° (5), 189° (7), 184° (5): note that this prod. appears to exist in two forms: when the lower-melting form is dislvd. in boilg. AcOH and pptd. with boilg. aq , or if it is allowed to solidify after fusion, the prod. has m.p. 191°; if the above AcOH soln. is slowly cooled, however, the prod. melts at 184° (5). [This tetranitro-C̄ htd. with NaOMe in MeOH yields 3,3'-dimethoxy-4,6,4',6'-tetranitrobiphenyl, m.p. 244° (5).] — [Note also that under some conditions (7) some 3,3'-dichloro-6,6'-dinitrobiphenyl [Beil. V-585, V_1-(274)], m p. 170° (8) (7), may form during nitration of C̄.]

C̄ on oxidn. with CrO_3 + V_2O_5 yields (3) *m*-chlorobenzoic acid (3:4392).

3:0180 (1) Weissberger, Sängewald, *Z. physik. Chem.* **B-20**, 155 (1933). (2) Ullmann, *Ann.* **332**, 54 (1904). (3) Bellavita, *Gazz. chim. ital.* **65**, 641 (1935). (4) Mascarelli, Gatti, *Gazz. chim ital.* **59**, 808–809 (1929). (5) van Alphen, *Rec. trav. chim.* **51**, 362–363 (1932). (6) Cain, *J. Chem. Soc.* **85**, 7 (1904). (7) Borsche, Scholten, *Ber.* **50**, 610 (1917). (8) Ullmann, Forgan, *Ber.* **34**, 3804 (1901).

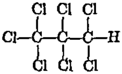
— 2,5-DICHLORO-2,5-DIMETHYL-HEXYNE-3 $C_8H_{12}Cl_2$ Beil. I —
I_1-(121)
I_2—



M.P. 29° B.P. 62–63° at 15 mm.

See 3:9504. *Division C: Liquids with b.p. reported only at reduced pressure.*

3:0200 1,1,1,2,2,3,3-HEPTACHLOROPROPANE C_3HCl_7 Beil. I - 108
(*unsym.*-Heptachloropropane) I_1-(35)
I_2-(73)



M.P. 29.40° (1) (4)	B.P. 247–248°	sl. dec. (3) (4)	D_4^{24} = 1.8048 (4)
29–30° (2) (3)	163–166°	at 90 mm. (5)	
30° (10)	150–151°	at 50 mm. (3)	
	147°	at 43 mm. (4)	
	137–140°	at 32 mm. (2)	
	122°	at 25 mm. (10)	
	110–113°	at 10 mm. (2)	

Hard cryst. with camphoraceous odor (3). [For crystallographic constants see (9).]

[For prepn. from tetrachloroethylene (3:5460) (or pentachloroethane (3:5880) (2) (3)) + $CHCl_3$ (3:5050) by condensation in presence of $AlCl_3$ (88–93% yield (2), 85% yield (1) (10)) see (1) (2) (5) (7); from pentachloroacetone (3:6205) by htg. with PCl_5 in s.t. at 180° for 6–8 hrs. see (3); from dichloroacetyl chloride (3:5290) with $AlCl_3$ on warming (CO + $CHCl_3$ + HCl are also formed) see (11).]

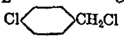
$\bar{C}$ has large mol. freezing-point lowering, viz., 120° (6). [For use in detn. of mol. wt. of org. compds. by f.p. lowering see (6).]

$\bar{C}$ on htg. especially in presence of catalysts such as $ZnCl_2$ yields HCl + hexachloropropene (3:6370); with CuCl a second reaction also occurs yielding HCl and tetrachloroethylene (3:5460). [For extensive study of these see (7) (8).]

$\bar{C}$ in alc. on titration with alk. gives (4) (3) an apparent Neut. Eq. of 285.5 because of loss of 1 HCl and formation of hexachloropropene (3:6370).

3:0200 (1) Prins, *Rec. trav. chim.* **54**, 249–252 (1935). (2) Farlow, *Org. Syntheses* **17**, 58–59 (1937). (3) Fritsch, *Ann.* **297**, 314 (1897). (4) Prins, *J. prakt. Chem.* **89**, 415–416 (1914). (5) Henne, Ladd, *J. Am. Chem. Soc.* **60**, 2491–2495 (1938). (6) Böeseken, Benedictus, *Rec. trav. chim.* **37**, 121–129 (1918). (7) Böeseken, van der Scheer, de Voogt, *Rec. trav. chim.* **34**, 78–95 (1915) [illegible] *chim. Belg.* **39**, 585–587 [illegible] 1).
(11) Böese [illegible] 466.

3:0220 *p*-CHLOROBENZYL CHLORIDE $C_7H_6Cl_2$ Beil. V - 297
V_1-(152)
V_2-(231)



M.P. 30° (1)	B.P. 217–218°	at 772 mm. (8)
29° (2) (3) (4)	214°	at 758 mm. (3)
(5) (6) (7) (35)	214°	(9) (10)
28.2–28.4° (12)	213–214°	(11)
26° (8)	114–117°	at 30 mm. (35)
	114°	at 25 mm. (12)
	113–115°	at 24 mm. (13)
	106.5–107.5°	at 23 mm. (14)
	117°	at 20 mm. (3)
	94–96°	at 14 mm. (8)

Cryst. from alc., AcOH or lgr. — Eas. sol. warm but less so cold alc., very eas. sol. ether, AcOH, C_6H_6, CS_2. — Sublimes at ord. temp. — At b.p. under ord. press. tends to decompose (7). — $\bar{C}$ has agreeable arom. odor, but strongly attacks mucous membrane (2).

[For prepn. of $\bar{C}$ from benzyl chloride (3:8535) with Cl_2 in pres. of I_2 (11) (8) (15) or $SbCl_5$ (16) see indic. refs.; from *p*-chlorotoluene (3:8287) with SO_2Cl_2 + Bz_2O_2 in dark (70% yield) (35), with Cl_2 in light (2) (17) (11) (5) (4) (18) (19) or with $PbCl_4.2NH_4Cl$ (9) see indic. refs.; from toluene with Cl_2 see (20); for prepn of $\bar{C}$ from chlorobenzene (3:7903) with CH_2O + HCl (36), with *bis*-(chloromethyl) ether (3.5245) or chloromethyl methyl ether (3:7085) (formed by use of formaldehyde or paraformaldehyde + chlorosulfonic acid + conc. H_2SO_4 or hexamethylenetetramine + conc. HCl (3)) as directed (50% yield (3)) (1) see indic. refs]

[$\bar{C}$ with phenol in toluene yields (21) 2-(*p*-chlorobenzyl)phenol, m.p. 60–61°, and *p*-chlorobenzyl phenyl ether, m.p. 85 5–86.5°; $\bar{C}$ with 2,4-dichlorophenol in toluene yields (21) 2-(*p*-chlorobenzyl)-4,6-dichlorophenol, m.p. 69.5–70.5°, and *p*-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 64.5–65 5°.]

[$\bar{C}$ with phenol + $AlCl_3$ yields (21) 4-(*p*-chlorobenzyl)phenol, m p. 87–87 5° (benzoate, m p. 115–116°); $\bar{C}$ with 2,6-dichlorophenol + $AlCl_3$ yields (21) 4-(*p*-chlorobenzyl)-2,6-dichlorophenol, m.p. 61.5–62 5° (benzoate, m p. 116–117°).]

[For condens. of $\bar{C}$ with *p*-chlorophenol (3:0475) and use of prod. as anti-moth prepn. see (22); for condens. of $\bar{C}$ with *o*-cresol (1:1400) or its Na salt or with 3,5-dimethylphenol (*sym-m*-xylenol)(1:1455) and use of products as bactericides see (23); for condens. of $\bar{C}$ with sulfonated phenol and use as tanning agent see (24); for condens. of $\bar{C}$ with resorcinol (1:1530) + $AlCl_3$ in nitrobenzene yielding 55% 4-(*p*-chlorobenzyl)resorcinol see (25).]

$\bar{C}$ with Mg in dry ether yields (10) p-$Cl.C_6H_4.CH_2$ MgCl which with phenyl isocyanate as directed (10) gives *p*-chlorophenylacetanilide [Beil. XII-275], lfts. from alc., m p. 168° cor. (26), 165–166° u.c. (10), 164.5° (27)

$\bar{C}$ on boilg. with aq. (2) (3) hydrolyzes to *p*-chlorobenzyl alc. [Beil. VI-444], m.p 70–71° (3) (for rate see (7)); $\bar{C}$ on boilg. with $Pb(NO_3)_2$ for 2 days (28) or on boilg in 60% alc. with hexamethylenetetramine (29) yields *p*-chlorobenzaldehyde (3:0765), m.p. 46–47° (3).

$\bar{C}$ with alc. KOH yields (30) *p*-chlorobenzyl ethyl ether [Beil. VI-444, VI_1-(222)], oil, b.p. 225° (for study of rate of reactn. see (31)); $\bar{C}$ with KOAc in abs. alc. yields (28) *p*-chlorobenzyl acetate [Beil. VI-445], b.p. 240° (28); $\bar{C}$ with boilg. alc. KCN yields (11) (28) (20) *p*-chlorobenzyl cyanide [Beil. IX-448], m p. 30° (20), b.p. 265–267° (20), which on hydrolysis yields *p*-chlorophenylacetic acid (3:3135), m p. 105° (20).

$\bar{C}$ with KI in alc. gives alm. quant. yield (17) *p*-chlorobenzyl iodide, m.p. 64° (17) (for study of rate of reactn. of $\bar{C}$ with NaI (34) or KI (14) (6) in acetone see indic. refs.); $\bar{C}$ with Na_2SO_3 yields (18) (13) sodium *p*-chlorotoluene-ω-sulfonate (corresp. sulfonamide, m.p. 157° (18), corresp. sulfonanilide, m p. 235° (18)).

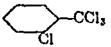
[$\bar{C}$ with thiourea (1 mole) in alc refluxed 30 min. gives (37) *S*-(*p*-chlorobenzyl)isothiourea hydrochloride (*p*-chlorobenzyl isothiuronium chloride), cryst. from 1:1 conc. HCl + aq., m p. 197°; this prod. is useful in identification of organic acids (37)]

$\bar{C}$ on oxidn. with CrO_3 (11) (3) or with $KMnO_4$ (1) (12) yields *p*-chlorobenzoic acid (3:4940), m p. 236°.

3:0220 [illegible] on, Field, *Ber.* **11**, 904–905 [illegible] (4) Jones, *J. Chem. Soc.* [illegible] 147 (1933). (6) Bennett, [illegible] . **41**, 307–308 (1921). (8) [illegible]gmann, Engel, *Z. physik. Chem.* **B-15**, 96 (1931–2). (9) Seyewetz, Trawitz, *Compt. rend.* **136**, 241 (1903). (10) [illegible]
(11) Beilstein, [illegible]
J. Am. Chem. Sc[illegible]
(14) Conant, Kir[illegible]
419–421 (1921). [illegible]
18, 388–392 (189[illegible]

... **1929**, II 1916. (20) von Walther, ...
... 4639–4643 (1933).
... (23) Klarmann, Gates (to Lehn and Fink, Inc), U.S. 1,926,873, 1,926,874, Sept. 12, 1933; *Cent.* **1934**, I 83. (24) I.G., Brit. 320,056, Oct. 31, 1929; *Cent.* **1930**, I 590; Brit. 321,190, Nov. 28, 1929; *Cent.* **1930**, I 1259. (25) Klarmann, von Wowern, *J. Am. Chem. Soc.* **51**, 608 (1929). (26) Jenkins, Richard- ... ner, *J. prakt. Chem.* (2) **62**, 562 (1900). (28) ... **117**, ...). (29) Mayer, English, *Ann.* **417**, 78–79 ... /63).
... **101**, 331–335 (1921). (32) Kindler, *Ann.* **452**, ... *prakt. Chem.* (2) **77**, 377–378 (1903). (34) ... h, Brown, *J. Am. Chem. Soc.* **61**, ... Oct. 8, 1933; *Cent.* **1931**, I 360 ... **61**, 3251–3252 (1939).

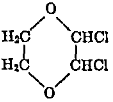
—— o-CHLOROBENZOTRICHLORIDE $C_7H_4Cl_4$ **Beil. V - 302**
V_1-(153)
V_2-(234)



M.P. 30° **B.P. 260°**

See 3:6880. *Division B: Liquids, Section* 1, $D_4^{20} > 1.15$.

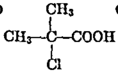
—— 2,3-DICHLORODIOXANE-1,4 $C_4H_6O_2Cl_2$ **Beil. S.N. 2668**



M.P. 30° **B.P. 100–101° at 24–25 mm.**

See 3:9105. *Division C: Liquids with b.p. only at reduced pressure.*

3:0235 α-CHLORO-ISOBUTYRIC ACID $C_4H_7O_2Cl$ **Beil. II-294**
II_1—
II_2—



M.P. 31° (1) (2)	**B.P. 118°**	at 50 mm. (1)
28–30° (3)	**116–118°**	at 50 mm. (4)
	80–82°	at 12 mm. (2)

Eas. sol. aq.

[For prepn. of C̄ from isobutyric acid (1:1030) with Cl_2 in light (5) (10) or with cat. as specified (6) (7), or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (15% C̄ + 85% β-chloro isomer) (3:9132) (3), see indic. refs.; from β,β,β-trichloro-*ter*-butyl alc. ("Chloretone") (3:2662) with aq alk. (small yield together with other prods.) see (1) (2); from 2-chloro-2-methylpropanol-1 (β-chloro-isobutyl alc.) (3:7305) by oxidn. with conc. HNO_3 see (8); from α-chloro-isobutyryl chloride (3:5385) by hydrolysis with aq. see (9).]

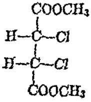
C̄ with aq. alk. yields (5) α-hydroxy-isobutyric acid (1:0431) together with other products. — C̄ with aq. $Ca(OCl)_2$ yields (4) chloroform (3:5050) + AcOH (1:1010) + CO_2.

C̄ with $SOCl_2$ (11) yields α-chloro-isobutyryl chloride (3:5385), b.p. 117–118°.

—— Methyl α-chloro-isobutyrate: b.p. 129° (see 3:7918).
—— Ethyl α-chloro-isobutyrate: b.p. 148° (see 3:8147).
—— α-Chloro-isobutyramide: unreported.
Ⓓ α-Chloro-isobutyr-anilide: m.p. 71–71.5° (3), 68° (12), 67–68° (13). [From α-chloro-isobutyryl chloride with aniline (3).] [Note that β-chloro-isobutyr-anilide has m.p. 109 0–109.5° (3).]
Ⓓ α-Chloro-isobutyro-p-toluidide: unreported.

3:0235 (1) Ostropjatow, *J. Russ. Phys.-Chem. Soc.* 28, 50 (1896), *Ber.* 29, Referate, 908–909 (1896). (2) Jacob, *Bull. soc. chim.* (5) 7, 581–586 (1940); *C.A.* 36, 3507 (1942). (3) Kharasch, Brown, *J. Am. Chem. Soc.* [illegible] 1216 [illegible] Dow [illegible] Loder, [illegible] (8) [illegible] kind, [illegible]

3:0240 DIMETHYL *meso*-α,α'-DICHLOROSUCCINATE $C_6H_8O_4Cl_2$ Beil. II-619 II_1— II_2—

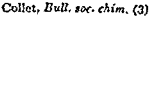


M.P. 31.5–32° (1)

[For prepn. of C̄ from *meso*-α,α'-dichlorosuccinic acid (3:4930) in MeOH with HCl gas see (1).]
[For studies on dipole moment see (2).]

3:0240 (1) Kirchhoff, *Ann.* 280, 215 (1894). (2) Hassel, Naeshagen, *Tids. Kemi Bergvesen* 10, 126–127 (1930); *Cent.* 1931, I 893, *C.A.* 25, 1493 (1931).

3:0245 2,5-DIMETHYLPHENACYL CHLORIDE $C_{10}H_{11}OCl$ Beil. VII-324 VII_1—
(ω-Chloro-2,5-dimethyl acetophenone)



M.P. 32°

[For prepn. from *p*-xylene, chloroacetyl chloride (3:5235) + $AlCl_3$, see (1) (2).]
C̄ on oxidn. with alk. $KMnO_4$ gives (2) trimellitic ac. (1:0551), m.p. 228°.

3:0245 (1) Kunckell, *Ber.* 30, 579 (1897). (2) Collet, *Bull. soc. chim.* (3) 17, 509 (1897).

[C̄ with liq. NH_3 as directed (39) gives 72% α-naphthylmethylamine (*N*-benzoyl deriv., lfts. from alc., m.p. 154° (1)) + 20% *bis*-(α-naphthylmethyl)amine (*N*-benzoyl deriv., pr. from alc., m.p. 134° (1)). — C̄ with alc. NH_3 as directed (39) gives 11% of the above prim. amine + 38% of the above sec. amine + 47% *tris*-(α-naphthylmethyl)amine, cryst. from alc., m.p. 178° (39). — Note the use of the above *bis*-(α-naphthylmethyl)amine as useful reagent for quant. pptn. of HNO_3 (6). — For reactn. of C̄ with $(CH_3)_2NH$ see (1). — C̄ with aniline at 100° gives (77% yield (4)) *N*-(α-naphthylmethyl)aniline, m.p. 67° (4) (corresp. nitroso cpd., m.p. 57° (4)).]

[C̄ with thiourea in alc. as directed (40) yields *S*-(α-naphthylmethyl)isothiourea hydrochloride, m.p. 238° (40). — C̄ with *p*-toluenesulfonamide + alc. KOH refluxed 12 hrs. gives (57% yield (6)) *N,N-bis*-(α-naphthylmethyl)*p*-toluenesulfonamide, cryst. from boilg. alc., m.p. 134° (6).]

[C̄ with various polynitrophenols gives addn. prods.: e g., that from picric acid has m.p. 80–82° (41), 84° (4); that from 2,4,6-trinitro-*m*-cresol has m.p. 81.5–82° (41); that from 2,4,6-trinitroresorcinol (styphnic acid) has m.p. 112.5–113° (41).]

Ⓓ *N*-(α-**Naphthylmethyl)phthalimide (ω-phthalimido-α-methylnaphthalene): white ndls.** from hot alc., m.p. 174–175° (6). [From C̄ + Na phthalimide refluxed 6 hrs. in alc. in 82% yield (6).] — [Hydrolysis of this prod. with 4 pts. conc. HCl in s.t. 2 hrs. at 100° gives (86% yield (6)) α-naphthylmethylamine (see above).]

3:0250 (1) von Braun, Moldaenke, *Ber.* **56,** 2167–2172 (1923). (2) Manske, Ledingham, *Can. J. Research* **17-B,** 14–20 (1939); *Cent.* **1939,** I 4037; *C.A.* **33,** 5387 (1939). (3) Darzens, Levy, *Compt. rend.* **202,** 73–75 (1936). (4) Anderson, Short, *J. Chem. Soc.* **1933,** 485. (5) de Pommereau, *Compt. rend.* **175,** 105–106 (1922). (6) Rupe, Brentano, *Helv. Chim. Acta* **19,** 581–586 (1936). (7) Reddelien, Lange (to I.G.), Ger. 508,890, Oct. 2, 1930; Brit. 337,289, Nov. 20,1930; *Cent.* **1931,** I 1830. (8) von Braun, Nelles, *Ber.* **66,** 1470 (1933). (9) Davies, Oxford, *J. Chem. Soc.* **1931,** 220–221. (10) Vavon, Bolle, Callin, *Bull. soc. chim.* (5) **6,** 1032–1033 (1939).

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(31) Briggs, Wilson, *J. Chem. Soc.* **1941,** 5
725–727 (1942); *C.A.* **37,** 5393 (1943). (33)
C.A. **27,** 81 (1933). (34) Deutsche Hydrier
4397. (35) I.G., French 811,273, April 10,
(to I.G.), Ger. 516,280, Jan. 21, 1931; *Cent.* **1931,** I 2396. (37) I.G., Brit. 462,290, April 1, 1937; *Cent.* **1937,** II 2456. (38) Kränzlein, Voss, Brunner, Ger. 526,391, June 5, 1931; *Cent.* **1931,** II 1203. (39) von Braun, *Ber.* **70,** 979–980, 983–984 (1937). (40) Sprague, Johnson, *J. Am. Chem. Soc.* **59,** 1839 (1937).

(41) Dermer, *Proc. Oklahoma Acad. Sci.* **22,** 160–162 (1941); *C.A.* **37,** 4376 (1943). (42) Izmail'skii, Kozin, *Compt. rend. acad. sci. U.R.S.S.* **28,** 621–624 (1940); *C.A.* **35,** 2882 (1941).
(43) Izmail'skii, *Compt rend.*
Grummitt, Buck, *Org. Synthes*
58, 28 (1936). (46) Shmuk,
39, 4069 (1945).

3:0255 *m*-CHLOROPHENOL

C_6H_5OCl

Beil. VI - 185
VI_1-(99)
VI_2-(172)

M.P. 32.8°	(1)	B.P. 215.5–217.1°	(7)	$D^{50}_{-} = 1.237$ (9)		$n^{40}_{D} = 1.5565$ (1)
32°	(2)	216°	(17)	$D^{25}_{-} = 1.268$ (9)		
31–32°	(3)	213–216°	(8)			
31°	(4)	214° (6) cor.	(16)			
28.5°	(5)	211–212° u.c.	(5)			
28°	(6)	98° at 12 mm.	(2)			

C̄ has odor like phenol (for study of strength of odor in aq soln. see (10)). — C̄ in pres. of aq. has unusual tendency to form supersatd. solns (11) (for temp./compn. data on soly. of C̄ in aq. or in C_6H_6 see (11)). — C̄ cas. discolors in air.

[For prepn. of C̄ from *m*-chloroaniline [Beil XII-602, XII_1-(300)] via diazotization and subsequent reaction with aq (yields: alm. quant. (12) (13), 67% (1), 64% (8), 55% (4), 50% (14)) (15) (5) (16) see indic. refs. (note that the process is sensitive to conditions and refs. indic. give valuable information on its control); for formn. of C̄ from *m*-dichlorobenzene (3:5960) with NaOMe in MeOH in s.t. at 180° for 30 hrs. see (17).]

C̄ like its isomers is sol. in conc. Na_2CO_3 soln at room temp and is repptd. by CO_2 (18). [For studies of value of ionization const. of C̄ in aq. or dil. MeOH or dil. EtOH see (19) (20) (6) (21) (22).]

C̄ on fusion with KOH yields (23) resorcinol (1:1530). — [For condens. of C̄ with phthalic anhydride to yield 3,6-dichlorofluorane ("fluorescein chloride") [Beil. XIX-147] (impt. intermed. in prepn of rhodamine dyes) see (12) (68).]

[C̄ conv. to dry Na salt and treated with CO_2 under press. yields after acidifn. (14) 6-carboxy-3-chlorophenol (4-chloro-2-hydroxybenzoic acid) (4-chlorosalicylic acid) (3.4908), ndls. from aq., m.p. 207° (14).]

[C̄ in the Reimer-Tiemann reactn. with alk. (or better $Ca(OH)_2 + Na_2CO_3$ (24)) and chloroform (24) or bromoform (25) yields both 6-aldehydo-3-chlorophenol (4-chlorosalicylaldehyde) (3.0960) and 4-aldehydo-3-chlorophenol (3 4280) in *o*/*p* ratio of 0.71 with $CHCl_3$ (26) (25) and 0.84 with $CHBr_3$ (25).] — [The 4-aldehydo-3-chlorophenol has also been obtd. (50% yield) from C̄ in C_6H_6 with HCl + HCN + ACl_3 (29).]

[C̄ in aq. Na_2CO_3 soln. couples with 1 equiv. of benzenediazonium chloride yielding (27) (18) 3-chloro-4-phenylazophenol, or.-yel. ndls. from 25% AcOH, m p. 95° (27), or, on expos. to HCl, or.-red, m p 114° (27) (18); C̄ in aq NaOH with 2 equivs. of benzenediazonium chloride yields (27) 3-chloro-2,4-*bis*(phenylazo)phenol, dark red-brn, m p. 181°; no *tris*-azo cpds. appear to be formed (27) — For study of coupling of C̄ with *p*-nitrobenzenediazonium bisulfate see (28).

[C̄ is *not* reduced by HI in AcOH (30); for study of replacement of Cl by H with H_2 + Ni cat. at room temp. see (31).]

[C̄ with *p*-aminophenol oxidized in alk. soln. with NaOCl yields (32) indochlorophenol; C̄ with *p*-aminodimethylaniline on oxidn with NaOCl as directed (8) yields 3-chloro-*N*,*N*-dimethylindoaniline.]

[For condensation of C̄ with formaldehyde (33) or with benzaldehyde-*o*-sulfonic acid (34) and use of product as mothproofing agents see indic refs.; for reactn. of C̄ with unsatd. halides in pres of alk. yielding *m*-chlorophenyl alkenyl ethers which by rearr. yield corresp. substituted phenols used as bactericides see (35) (36).]

[For condens. of C̄ with malic acid (1.0450) + conc. H_2SO_4 giving small yield of 7-chlorocoumarin [Beil. XVII-331] see (37); with ethyl acetoacetate (1:1710) + H_2SO_4

giving small yield of 7-chloro-4-methylcoumarin [Beil. XVII-336] see (37); with ethyl methylacetoacetate (1:1712) + P_2O_5 yielding 7-chloro-2,3-dimethylchromone [Beil. $XVII_1$-(177)] see (38).]

$\bar{C}$ with 3 moles Br_2 (in aq. KBr) gives 100% yield (39) 2,4,6-tribromo-3-chlorophenol, ndls. from dil. alc., m.p. 105–106° cor. (39) (methyl ether, m.p. 96° (39)); $\bar{C}$ in 10% aq. KOH with 4 moles I_2 (in aq. KI) gives 2,4,6-triiodo-3-chlorophenol, ndls. from boilg. AcOH, m.p. 139–140° (39).

[$\bar{C}$ in dil. NaOH mixed with aq. $NaNO_2$ and acidified as directed (40) gives (40% yield (40)) (43) 3-chloro-4-nitrosophenol, m.p. 133° (40), 129.6° (41); on soln. in Na_2CO_3 and subsequent acidification this cpd. yields (40) (43) the isomeric 3-chlorobenzoquinone-4-monoxime, m.p. 184° dec. (40), cf. (42).]

[$\bar{C}$ on mononitration with H_2SO_4 + $NaNO_3$ as directed (44) or $\bar{C}$ in AcOH with fumg. HNO_3 at 0° (45) gives (yield: 32% (45), 22% (44)) 3-chloro-6-nitrophenol [Beil. VI-238], volatile with steam, m.p. 41° (44), together with (60% yield (44)) 3-chloro-4-nitrophenol [Beil. VI-240], not volatile with steam, white ndls. from dil. HCl or aq., m.p. 121–122° (44). — Note that the two other position isomers although known have been obtd. indirectly: 3-chloro-2-nitrophenol, anhydrous form, yel. cryst., m.p. 45–47° (46) (47); monohydrate, colorless cryst. from pet. ether, m.p. 37.5–38° (46) (47) (44); 3-chloro-5-nitrophenol [Beil. VI-239] (48), m.p. 147°.]

[$\bar{C}$ on dinitration as directed (44) (49) gives 3-chloro-4,6-dinitrophenol [Beil. VI-259, VI_1-(128)], colorless cryst. from aq. or lt. pet., m.p. 92–93° (44). — Note that two other position isomers are known but prepd. indirectly: 3-chloro-2,6-dinitrophenol, white cryst. from dil. HCl, m.p. 114.5° (44) (49); 3-chloro-2,4-dinitrophenol, cryst. from aq., m.p. 138–140° (44) (49).]

$\bar{C}$ on trinitration by soln. in 1½ pts. fumg. H_2SO_4 (27% SO_3) and treated in cold for 1 hr. with 10 pts. 70% HNO_3 (44) cf. (4) (50) yields 3-chloro-2,4,6-trinitrophenol [Beil. VI-292], cryst. from aq. or dil. H_2SO_4, m.p. 114° (44), 116° (4), 119° (50). — [Note that if $\bar{C}$ is sulfonated prior to trinitration the isomeric 3-chloro-2,5,6-trinitrophenol, m.p. 112.5–113.5° (44), is obtd. (44).]

[For studies on the sulfonation of $\bar{C}$ see (44) (51) (52) (53).]

[$\bar{C}$ in MeOH/KOH with MeI yields (29) m-chlorophenyl methyl ether (m-chloroanisole) (8:6195).] [$\bar{C}$ in EtOH/KOH with EtI gives (18) 3-chlorophenyl ethyl ether (m-chlorophenetole) (3:6323), b.p. 204–205° at 717 mm., D_4^{20} = 1.1712 (18) (for rate of formn. from sodium salt of $\bar{C}$ with EtI in alc. soln. see (55)).]

—— **m-Chlorophenyl acetate** [Beil. VI-185]: oil, b.p. 116.5° at 21 mm. (18), 108° at 12 mm. (57), 84–86° at 2 mm. (57), m.p. −1.5° to −0.5° (18), D_4^{20} = 1.2209 (18). [From $\bar{C}$ with Ac_2O + NaOAc (18) or indirectly from m-chloroaniline via diazotization, etc. (57).] [For rate of reactn. of $\bar{C}$ with AcBr see (58).]

Ⓓ **m-Chlorophenyl benzoate** [Beil. IX-117]: pr. from dil. alc. or dil. acetone, m.p. 71–72° (18). [From $\bar{C}$ in 10% aq. Na_2CO_3 with BzCl (18); for study of rate of benzoylation of $\bar{C}$ see (59).]

Ⓓ **m-Chlorophenyl m-nitrobenzoate**: ndls. from alc. or dil. acetone, m.p. 94–95° (18). [From $\bar{C}$ in alk. with m-nitrobenzoyl chloride (18).]

Ⓓ **m-Chlorophenyl p-nitrobenzoate**: m.p. 99°.

Ⓓ **m-Chlorophenyl 3,5-dinitrobenzoate**: m p. 156°.

—— **m-Chlorophenyl benzenesulfonate**: unrecorded.

—— **m-Chlorophenyl p-toluenesulfonate**: unrecorded.

—— **m-Chlorophenyl benzyl ether**: m.p. 59°. [From $\bar{C}$ + benzyl-phenyl-dimethyl-ammonium chloride (60).]

—— **m-Chlorophenyl p-nitrobenzyl ether**: unrecorded.

—— *m*-**Chlorophenyl 2,4-dinitrophenyl ether:** pale yel. ndls. from alc., m.p. 75° (61). [From C̄ in alk. with alc. 2,4-dinitrochlorobenzene (61).]

Ⓓ *m*-**Chlorophenoxyacetic acid:** cryst. from aq., m.p. 108–110° u.c. (62), Neut. Equiv. 186.5. [From C̄ in aq. NaOH with chloracetic acid (62).]

—— *m*-**Chlorophenyl *N*-phenylcarbamate:** unrecorded.

Ⓓ *m*-**Chlorophenyl *N*-(*p*-bromophenyl)carbamate:** ndls. from C_6H_6 + EtOAc, m.p. 121–123° cor. (64). [From C̄ + *p*-bromobenzazide in lgr. (64).]

Ⓓ *m*-**Chlorophenyl *N*-(*p*-iodophenyl)carbamate:** m.p. 138–139° (69). [From C̄ with *p*-iodobenzazide in hot lgr. (69).]

Ⓓ *m*-**Chlorophenyl *N*-(*m*-nitrophenyl)carbamate:** m.p. 115–116° u.c., 117–118° cor. (70). [From C̄ with *m*-nitrobenzazide or with *m*-nitrophenyl isocyanate in lgr. (70).]

Ⓓ *m*-**Chlorophenyl *N*-(*p*-nitrophenyl)carbamate:** pale yel. pr. from lgr., m.p. 144° cor. (65). [From C̄ + *p*-nitrobenzazide in lgr. (65).]

Ⓓ *m*-**Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate:** or.-yel. pr. from lgr., m.p. 170–172° u.c., 174–176° cor. (63). [From C̄ with 3,5-dinitro-4-methylbenzazide in lgr. (63).]

Ⓓ *m*-**Chlorophenyl *N*-(α-naphthyl)carbamate:** cryst. from lgr., m.p. 157–158° (66). [From C̄ + α-naphthyl isocyanate in lgr. (66).]

Ⓓ *m*-**Chlorophenyl *N*-(β-naphthyl)carbamate:** pr. from lgr., m.p. 114–115° u.c., 116–117° cor. (67). [From C̄ + β-naphthyl isocyanate (or azide) in lgr. (67).]

—— *m*-**Chlorophenyl *N*,*N*-diphenylcarbamate:** unreported.

3:0255 (1) Holleman, Rinkes, *Rec. trav. chim.* **30**, 81–82, 86 (1911), **42**, 1092 (1923). (2) Kuhn, Wassermann, *Helv. Chim. Acta* **11**, 14 (1928). (3) Williams, Fogelberg, *J. Am. Chem. Soc.* **52**, 1358 (1930). (4) Seekles, *Rec. trav. chim.* **42**, 76–77 (1923). (5) Uhlemann, *Ber.* **11**, 1161–1162 (1878). (6) Bennett, Brooks, Glasstone, *J. Chem. Soc.* **1935**, 1823. (7) Kohlrausch, Pongratz, *Monatsh.* **65**, 202 (1935). (8) Fieser, Thompson, *J. Am. Chem. Soc.* **61**, 382–383 (1939). (9) Thole, Mussell, Dunstan, *J. Chem. Soc.* **101**, 1115 (1913). (10) Holleman, *Rec. trav. chim.* **37**, 106 (1918).

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(51) Hodgson, Kershaw, *J. Chem. Soc.* **1930**, 1419–1425, **1929**, 2918, 2923. (52) Schoepfle,

Van Natta, Clarkson, *J. Am. Chem. Soc.*
58, 2734 (1925). (54) Ghaswalla, Donn
Chem. Soc. **1926**, 1254. (56) Réverdin, E
J. Am. Chem. Soc. **55**, 4954–4955 (1933);
Bassett, *J. Chem. Soc.* **1931**, 2516–2518. (59) Bernoulli, St. Goar, *Helv. Chim. Acta* **9**, 755 (1926). (60) Baw, *J. Indian Chem. Soc.* **3**, 101–104 (1926).

(61) Bost, Nicholson, *J. Am. Chem. Soc.* **57**, 2368–2369 (1935). (62) Koelsch, *J. Am. Chem. Soc.* **53**, 304–305 (1931). (63) Sah, *Rec. trav. chim.* **58**, 587–588 (1939). (64) Sah, Cheng, *Rec. trav. chim.* **58**, 592–593 (1939). (65) Sah, Cheng, *Rec. trav. chim.* **58**, 596–599 (1939). (66) French, Wirtel, *J. Am. Chem. Soc.* **48**, 1736–1739 (1926). (67) Sah, *Rec. trav. chim.* **58**, 454–458 (1939). (68) British Dyestuffs Corp., Ltd., & Hodgson, Brit. 205,254, Nov. 8, 1923; *Cent.* **1924**, I 711. (69) Sah, Young, *Rec. trav. chim.* **59**, 357–363 (1940). (70) Sah, Woo, *Rec. trav. chim.* **58**, 1014–1015 (1939).

3:0270 *d,l*-β-CHLORO-*n*-VALERIC ACID $C_5H_9O_2Cl$ Beil. S.N. 162

$CH_3.CH_2.CH(Cl).CH_2.COOH$

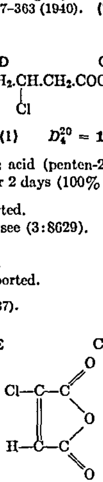
M.P. 33° (1) **B.P. 112° at 10 mm. (1)** D_4^{20} = **1.1484 (1)** n_D^{20} = **1.4462 (1)**

[For prepn. of C̄ from propylidene-acetic acid (penten-2-oic acid-1) [Beil. II-426, II_1-(191), II_2-(399)] with dry HCl gas at 20° for 2 days (100% yield) see (1).]

—— Methyl β-chloro-*n*-valerate: unreported.
—— Ethyl β-chloro-*n*-valerate: b.p. 189° see (3:8629).
—— β-Chloro-*n*-valeramide: unreported.
—— β-Chloro-*n*-valeranilide: unreported.
—— β-Chloro-*n*-valero-*p*-toluidide: unreported.

3:0270 (1) Schjanberg, *Ber.* **70**, 2385–2391 (1937).

3:0280 CHLOROMALEIC ANHYDRIDE C_4HO_3Cl Beil. XVII-434 $XVII_1$—



M.P.	B.P.			
33° (1)	196.3° cor. (2)		D_{25}^{25} = 1.5421 (2)	$n_{He}^{16.7}$ = 1.50594 (1)
34.5° (2) (3)	194°		D_4^{15} = 1.5427 (1)	$n_{He}^{13.9}$ = 1.50933 (1)
	150–151°	at 210 mm. (2)		
	95°	at 25 mm. (3A)		
	87°	at 14 mm. (1)		
	78°	at 8 mm. (1)		

C̄ usually observed as a colorless oil. On cooling and scratching it solidifies to a cryst. mass fusing about 0° and suddenly changing to a hard cryst. form, m.p. 34.5°, with evoln. of ht. (2) (3).

[For prepn. from chlorofumaric ac. (3:4853) by distn. with P_2O_5 see (1) (4), by distn. with $POCl_3$ see (5) (such products are claimed by (1) to be impure); for prepn. by distn. with AcCl see (2); for still other methods see Beil. XVII-434.]

[For Diels-Alder addn. of C̄ to cyclopentadiene-1,3 (1:8030) giving 71% yield of prod. m.p. 161°, or to anthracene (1:7285), giving 56% yield of prod., m p. 157°, see (7); note, however, that C̄ with isoeugenol (1:1785) or with isosafrole (1·7610) not only adds but also loses HCl giving (8) derivs. of 3-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic anhydride.]

C̄ reacts with aq. evolving ht. and upon evapn. yields (3) (3A) (6) chloromaleic ac. (3:3432), cryst. from mixt. of $CHCl_3$ + AcOH (6), which after drying at 100° have m.p. 114–115° (6).

3:0280 (1) von Auwers, Harres, *Ber.* **62**, 1686–1687 (1929). (2) Perkin, *J Chem. Soc.* **53**, 703–705 (1888). (3) van der Riet, *Ann.* **280**, 227 (1894) (3A) Zincke, Fuchs, *Ber* **26**, 508 (1893). (4) Walden, *Ber.* **30**, 2885–2886 (1897). (5) Thomas-Mamert, *Bull. soc chim.* (3) **13**, 847 (1895). (6) Michael, Tissot, *J. prakt Chem.* (2) **52**, 331 (1895) (7) Synerholm, *J. Am. Chem Soc.* **67**, 1229–1230 (1945). (8) Synerholm, *J. Am. Chem. Soc.* **67**, 345 (1945)

3:0290 TRICHLOROMETHYL TRICHLOROACETATE $C_3O_2Cl_6$ Beil. III -17
(Perchloromethyl acetate) $Cl_3C.O.CO.CCl_3$ III_1—
III_2—

M.P. 34° (1) **B.P. 191–192°** (1) D_4^{35} = **1.67331** (1)
73–74° at 10 mm. (1)

Sol. without decompn. in ether, $CHCl_3$, C_6H_6, or pet. eth.

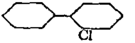
[For prepn. (71% yield (3)) by electrolysis of potassium trichloroacetate (3) or mixt of Na and Zn trichloroacetates (2) (4) see (2) (3) (4); *for formn. from methyl trichloroacetate* on chlorination see (1).]

C̄ with aq. decomposes to trichloroacetic acid (3·1150) + phosgene (3:5000) + HCl (2) (4).

C̄ with aniline yields *N,N'*-diphenylurea + aniline trichloroacetate + aniline hydrochloride (2).

C̄ with $AlCl_3$ yields hexachloroethane (3.4835) + CO_2 (5).

3:0290 (1) Anschütz, Emery, *Ann.* **273**, 59 (1893) (2) Elbs, Kratz, *J. prakt. Chem.* (2) **55**, 502–505 (1897). (3) Gibson, *Proc. Roy. Soc Edinburgh* **44**, II 140–152 (1924); *C.A.* **18**, 3041 (1924). (4) Fichter, Fritsch, Müller, *Helv. Chim. Acta* **6**, 506 (1933). (5) Jaeger, *Cent.* **1912**, I 1817.

3:0300 2-CHLOROBIPHENYL  $C_{12}H_9Cl$ Beil. V - 579
(2-Chloro-xenene (1)) V_1-(272)
V_2-(483)

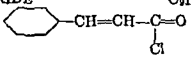
M.P. 34°	(2) (3) (4) (5)	**B.P. 273.7–273.8°**	at 738 mm.	(7)
33°	(6)	**267–268°**		(2)
32.2°	(7)	**210–211°**	at 150 mm.	(8)
31°	(15)	**165–170°**	at 28 mm.	(3)
		154°	at 12.5 mm.	(15)
		150–155°	at 10 mm.	(5)

Cryst. from alc. — Volatile with steam (6). — Sol. alc., CCl_4 (7); very sol. C_6H_6 or pet. eth. (2).

[For prepn. (36.8% yield (7)) (together with other products) from biphenyl by direct chlorination in presence of Fe or other cat. see (7) (2) (8) (9); for prepn. (25–38% yield (5)) from diazotized *o*-chloroaniline + C_6H_6 see (5) (4); for prepn. (60% yield (15)) from diazotized *o*-aminobiphenyl via Cu_2Cl_2 method see (15) (10).]

3:0330 CINNAMOYL CHLORIDE C_9H_7OCl Beil. IX - 587

IX_1-(233)



M.P.		B.P.			
36°	(1) (2)	257.5°	at 760 mm.	(2)	$D_4^{45.3}$ = 1.1617 (15)
35-36°	(3) (4)	251-253°		(1)	$n_D^{42.5}$ = 1.61364 (15)
	(5) (6)	170-171°	at 58 mm.	(9)	$D_{-}^{37.6}$ = 1.1632 (7)
	(9)	154° u.c.	at 25 mm.	(6)	$n_D^{37.6}$ = 1.6202 (7)
35°	(7) (14)	131°	at 20 mm.	(15)	
34°	(8)	147°	at 16 mm.	(10)	
		136-137°	at 15 mm.	(3) (5)	
		130°	at 14 mm.	(11)	
		130°	at 12 mm.	(4) (12)	
		136°	at 11 mm.	(13)	
		131°	at 11 mm.	(14)	
		127.3-127.6°	at 10 mm.	(8)	
		122-123°	at 8 mm.	(15)	
		101°	at 2 mm.	(16)	

White cryst., sol. in CCl_4 and in pet. eth. — Note that the name cinnamoyl chloride avoids confusion with cinnamyl chloride, $C_6H_5.CH{=}CH.CH_2Cl$ (3:0010).

[For prepn. of C̄ from cinnam
PCl_3 (19) (15) (6), with PCl_3 + [illegible]
90-95% (13), 89% (11)) (62) (1 [illegible]
in pres. of tertiary bases (20), with p-toluenesulfonyl chloride in pyridine or diethylaniline
[illegible] innamic acid (1:0735) with oxalyl (di)chloride
[illegible]
[illegible] oily prod. which with aq. hydrolyzes to a mixt. of cinnamic acid dichloride [Beil. IX-514, IX_1-(200)], m.p. 167°, and allocinnamic acid dichloride [Beil. IX-514], m.p. 84°; C̄ in CCl_4 with Cl_2 in direct sunlight, however, yields (5) α,β-dichloro-β-phenylpropionyl chloride (the acid chloride of cinnamic acid dichloride), ndls. from pet. eth., m.p. 54-55° (5), 55° (23).]

[C̄ is not reduced by copper hydride (24) but on cat. hydrogenation as directed (25) (26) yields cinnamaldehyde (1:0245).] [C̄ with KCN + quinoline gives (34% yield (57)) 1-cinnamoyl-2-cyano-1,2-dihydroquinoline which on acid hydrolysis yields 30% cinnamaldehyde (1:0245).]

[C̄ with 5% H_2O_2 in acetone + pyridine yields (27) di-cinnamoyl peroxide, m.p. 144° (27).]

[C̄ with anhydrous neutral K oxalate (28), or with dil. aq. KOH + methylaniline or dimethylaniline (29) or with pyridine (30), or with excess $K_2S_2O_5$ in pyridine (31), or with Na cinnamate (6), yields cinnamic anhydride [Beil. IX-586, IX_1-(232)], ndls. from C_6H_6 or alc., m.p. 136° (30).] — [C̄ with aq. under certain conditions yields cinnamic anhydride + HCl (for use in micro detn. of aq. (2), or indirectly for micro detn. of O_2 (after combustion), see (4) (32)).]

[For reactn. of C̄ with diethyl malonate (1 mole) + Na (2 moles) see (33); for reactn. of C̄ with ethyl sodio-acetoacetate giving (60% yield (10)) (34) ethyl *α-cinnamoylacetoacetate*, m.p. 44° (10) (Cu enolate, m.p. 164° (10)), with methyl sodio-acetoacetate giving (35) methyl α-cinnamoylacetoacetate, m.p. 49-50° (35), with ethyl sodio-benzoylacetate giving (10) ethyl cinnamoyl-benzoyl-acetate (*Cu enolate, m p. 202° (10)*), or with sodio-benzoylacetone giving (36) benzoyl-cinnamoyl-methane, m.p. 111° u.c. (36), see indic. refs.]

[$\bar{C}$ with C_6H_6 + $AlCl_3$ in CS_2 gives (37) (38) (39) (41) (by combined ring closure and addition to the unsatd. linkage or vice versa) 3-phenylhydrindone-1 (3-phenylindanone-1) [Beil. VII-483, VII_1-(265)], cryst. from MeOH, m.p. 78° (37), 77–78° (39) (oxime, m.p. 141° (40), phenylhydrazone, m.p. 130° (40), *p*-nitrophenylhydrazone, m.p. 220–221° (39), semicarbazone, m p. 223–225° (39)), accompanied by *β,β*-diphenyl-propiophenone (1,3,3-triphenylpropanone-1) [Beil. VII-524, VII_1-(293)] (38) *and other prods.: note that under* similar conds (41) with toluene or *o*-xylene neither of the corresp. indanones is formed (see also below); however, $\bar{C}$ + *m*-xylene + $AlCl_3$ in CS_2 yields (41) 5,7-dimethyl-3-phenylindanone-1, m p. 101° (semicarbazone, m.p. 195–197° (41)), and $\bar{C}$ + *p*-xylene + $AlCl_3$ in CS_2 yields (41) 4,7-dimethyl-3-phenylindanone-1, m p 94–95° (oxime, m.p. 218–219°; phenylhydrazone, m p. 193–194°; semicarbazone, m.p. 232° (41)).]

[$\bar{C}$ with many arom. cpds. in pres. of $AlCl_3$ condenses with loss of HCl to yield corresp. benzalacetophenone (chalcone) derivs.: $\bar{C}$ with C_6H_6 + $AlCl_3$, however, gives no (41) chalcone (see above); $\bar{C}$ with toluene + $AlCl_3$ yields (41) 4′-methylchalco… ; $\bar{C}$ with *o*-xylene + $AlCl_3$ in CS_2 gives (63% yield (41)) 3′,4′… , (41), $\bar{C}$ with *m*-xylene + $AlCl_3$ in CS_2 yiel… at 11 mm. (41); $\bar{C}$ with biphenyl + … 4′-phenylchalcone, m p. 155–156° (45), 165° (11…

[Similar chalcone formation occurs w… …ny arom. ethers; e g., $\bar{C}$ with anisole + $AlCl_3$ in CS_2 gives (42) 4′-methoxychalcone [Beil. VIII-193, $VIII_1$-(580)], m.p. 106–107° (42); $\bar{C}$ similarly with phenetole gives (42) 4′-ethoxychalcone [Beil. VIII-193], m p. 74–75° (42); $\bar{C}$ similarly with methyl *p*-tolyl ether gives (43) not only 2′-methoxy-5′-methylchalcone, m.p. 55–56°, but also by demethylation 2′-hydroxy-5′-methylchalcone, m p. 111° (43); $\bar{C}$ similarly with methyl 3,4-dimethylphenyl ether yields (13) 4′,5′-dimethyl-2′-methoxychalcone, m p. 78° (13); *$\bar{C}$ similarly with methyl β-naphthyl ether yields (44) β-methoxy*-naphthochalcone, m p 138–140° (44); $\bar{C}$ similarly with diphenyl ether yields (37) 4′-phenoxychalcone, m p 85° (37): for extension of this reactn. to ethers of polyhydric phenols such as $\bar{C}$ + $AlCl_3$ + *catechol dimethyl ether (veratrole) (1:7560) (44), resorcinol dimethyl* ether (1:7570) (13), resorcinol diethyl ether (1·7585) (13) (43), hydroquinone diethyl ether (1:7185) (43), and pyrogallol trimethyl ether (1.7145) (44) see indic. refs.]

[Similar formation of substituted chalcones occurs with $\bar{C}$ + $AlCl_3$ + phenols; e.g., for cases of $\bar{C}$ with *o*-cresol (1:1400) (46), resorcinol (1:1530) (47), phloroglucinol (1:1620) *(47) cf. (48) see indic. refs.]*

[$\bar{C}$ with diazomethane in ether gives (49) (50) (note both replacement of Cl and addn. to unsatd. linkage) 5-(diazoacetyl)-4-phenylpyrazoline, cryst. from C_6H_6 + pet. eth.; m.p. 80–81° (49), 77–78° (50)]

[$\bar{C}$ + NaN_3 in ether gives (12% yield (51)) (52) cinnamoyl azide, cryst. from lgr., m p. 86° dec. (51) (52); this cpd. on htg above m p or preferably in C_6H_6 readily loses N_2 and rearr. giving (77% yield (53)) (51) (52) styryl isocyanate, b p. 107° at 12 mm.; this isocyanate (or even its azide precursor) with aq at 50° yields (51) *N,N′*-distyrylurea, m p. 213–214° (51); for its reactn. with MeOH *yielding (52) methyl N-styrylcarbamate, m.p. 126°, with* EtOH yielding (52) ethyl *N*-styrylcarbamate, m p. 87°, with ammonia gas in dry ether yielding (51) *N*-styrylurea, m p 143°, or with aniline yielding (52) *N*-phenyl-*N*-styrylurea, m.p. 217°, see indic. refs.]

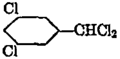
[$\bar{C}$ with free NH_2OH in C_6H_6 gives (100% yield (16)) cinnamoylhydroxamic acid, cryst. from hot EtOAc by addn. of lgr , m p. 119.5° (16), 111.5° (54)]

[$\bar{C}$ htd. with urea at 70° gives (44% yield (55)) (56) *N*-cinnamoylurea, m.p. 208–209° (55), 197° (56).]

[For reactn. of $\bar{C}$ with C_6H_5MgBr see (58); for reactn. of $\bar{C}$ with cellulose see (59); for reactn. with *o*-aminothiophenol yielding 1-styrylbenzothiazole see (60); for reactn. of $\bar{C}$

3:0360 (1) Hinkel, Hey, *J. Chem. Soc.* **1928**, 2786–2791. (2) Scarborough, Waters, *J. Chem. Soc.* **1927**, 93.

3:0370 3,5-DICHLOROBENZAL (DI)CHLORIDE $C_7H_4Cl_4$ **Beil. S.N. 466**



M.P. 36.5° (1)

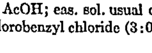
Colorless cryst. from MeOH or from dil. AcOH; eas. sol. usual org. solv. [Note that C̄ has same m.p. as the closely related 3,5-dichlorobenzyl chloride (3:0350) but that a mixture of the two becomes liquid.]

[For prepn. of C̄ from 3,5-dichlorobenzaldehyde (3:1475) with PCl_5 (80% yield) see (1).]

C̄ on hydrolysis with fumg. H_2SO_4 as directed gives (71–80% yield (1)) 3,5-dichlorobenzaldehyde (3:1475) (for study of rate of hydrol. in 50% alc. at 83.5° see (2)).

3:0370 (1) Asinger, Lock, *Monatsh.* **62**, 347 (1933). (2) Asinger, Lock, *Monatsh.* **62**, 337–338 (1933).

3:0372 2,4,6-TRIMETHYLBENZYL CHLORIDE $C_{10}H_{13}Cl$ **Beil. S.N. 469**
(α^2-Chloroisodurene)



M.P. 37° (1) (2) (3) (4) B.P. 130–131° at 22 mm. (1)
121–123° at 19 mm. (2)
119° at 15 mm. (4)
114–115° at 10 mm. (3)

[*See also the isomeric* 2,4,5-*trimethylbenzyl chloride* (3:9702).]

Colorless cryst. from alc. (4). — C̄ blisters skin (3). — [Equiv. conductance of C̄ in liq. SO_2 is 10 times that of benzyl chloride (3:8535) (3) cf. (5).]

PREPARATION OF C̄

[For prepn. of C̄ from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with formalin (1:0145) + conc. HCl + HCl gas at 55° for 5½ hrs. (yields: 55–61% (1), 29% (3)) (some α^2,α^4-dichloropentamethylbenzene = *bis*-1,3-(chloromethyl)2,4,6-trimethylbenzene, cryst. from pet. eth., m.p. 105° (1) (3), is also formed) see indic. refs.]

[For prepn. of C̄ from mesitylene (1:7455) with chloromethyl methyl ether (3:7085) + $SnCl_4$ (yields: 60% (4) cf. (6)), or in AcOH without other cat. (yields: 80–85% (7), 80% (2)), or with chloromethyl ethyl ether (3:7195) + $SnCl_4$ in CCl_4 soln. at −5° (70% yield (8)), see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Reduction. [C̄ with H_2 + Pt cat. in alc. soln. gives (80% yield (2) cf. (7)) 1,2,3,5-tetramethylbenzene (isodurene) [Beil. V-430, V_2-(329)] (9), liquid, b.p. 195–197° at 760 mm., f.p. −24°, $D_4^{20} = 0.8906$.]

Hydrolysis. C̄ on hydrolysis (no details (2)) gives 2,4,6-trimethylbenzyl alc. (mesitylcarbinol), ndls. from alc., m.p. 89° (2), 88–89° (10) (3) (11), 87° (12) (corresp. *N*-phenylcarbamate, m.p. 124–125° (11)).

Conversion to ethers. [$\bar{C}$ with MeOH/KOH at 100° for 3 hrs. gives (79% yield (3)) methyl 2,4,6-trimethylbenzyl ether, oil, b.p. 109–110° at 15 mm. (3), $\bar{C}$ with EtOH/KOH similarly gives (77% yield (3)) ethyl 2,4,6-trimethylbenzyl ether, oil, b.p. 114–115° at 14 mm. (3).]

Conversion to esters. [$\bar{C}$ with AgOAc in AcOH at 100° for 3 hrs. gives (70% yield (3)) 2,4,6-trimethylbenzyl acetate, oil, b.p. 136–137° at 15 mm. (3); this ester on hydrolysis with 15% aq. KOH at 100° for 3 hrs. gives (91% yield (3)) 2,4,6-trimethylbenzyl alc., m.p. 88–89°. (See also above.)]

Conversion to nitrile. $\bar{C}$ in alc. with aq. NaCN (1) (13) or KCN (4) (8), or C with CuCN in pyridine (14) cf. (1), gives (yields: almost 100% (13), 89–93% (1)) mesitylacetonitrile, cryst. from pet. eth., m p. 79–80° (1), 79° (4); b p. 160–165° at 22 mm. (13), 150–155° at 15 mm. (4), 190° at 11 mm. (8); this nitrile on hydrolysis with abt. 50% H_2SO_4 under reflux for 6 hrs. gives (87% yield (1)) mesitylacetic acid [Beil. IX-563, IX_1-(219)], cryst. from dil. alc. or lgr., m.p. 167–168° (1) (note that partial hydrolysis may give mesitylacetamide, m p. 216° (8)).

Behavior of $\bar{C}$ with Organometallic Compounds

With MeMgI. [$\bar{C}$ with MeMgI in dry ether undergoes mainly a coupling reaction giving (86% yield (15)) 1,2-dimesitylethane, m.p. 117.0–117.5°, accompanied by a little ethylmesitylene (1-ethyl-2,4,6-trimethylbenzene), b p 212–214° (15), 210° at 725 mm. (16), D_{20}^{20} = 0.894 (16), n_D^{20} = 1.5074 (16) (corresp. dinitro deriv., m.p. 111° (17), 109–111° (17) (15)).]

With misc. reactants. [$\bar{C}$ with diethyl sodiomalonate gives (4) diethyl α-(2,4,6-trimethylbenzyl)malonate, m.p. 36°, b p. 195–197° at 15 mm. (4). — $\bar{C}$ with ethyl sodiobenzoylacetate gives (21% yield (18)) ethyl α-(2,4,6-trimethylbenzyl)benzoylacetate which upon alk. hydrolysis gives (45% yield (18)) the ketone 1-benzoyl-2-mesitylethane, ndls. from MeOH, m.p. 85.0–85.5° (18).]

Other Reactions of $\bar{C}$

[$\bar{C}$ (1 mole) with hexamethylenediamine (1 mole) in $CHCl_3$ refluxed 3 hrs. gives (96% yield (19)) corresp. quaternary salt, $\bar{C}.C_6H_{12}N_4$: this prod. in aq. refluxed 4 hrs does *not* give the expected mesitaldehyde but instead (75% yield (19)) di-(2,4,6-trimethylbenzylamino)methane, cryst. from alc., m.p. 151.5–152° (19)]

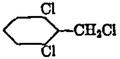
Ⓓ *N*-(2,4,6-Trimethylbenzyl)phthalimide: ndls. from alc., m p. 209.5–210° (19). [From $\bar{C}$ with K phthalimide at 170–180° for 4 hrs. as directed (19) (63% yield (19)).]

3:0372 (1) Fuson, Rabjohn, *Org. Syntheses* **25**, 65–68 (1945) ... *chim.* (5) **6**, 1025–1033 (1939). (3) Nauta, Diensk ... (4) Hoch, *Compt. rend.* **192**, 1465–1466 (1931). (5) N ... (6) Sommelet, *Compt. rend.* **157**, 1443 (1913). (7) ... (1937). (8) Sordes, *Compt rend.* **195**, 248–249 (193 ... **2** (1st ed), 360–362 (1943); **11**, 66–69 (1931). (10) Fuson, Southwick, Rowland, *J. Am. Chem. Soc.* **66**, 1112 (1944).

(11) Carre, *Bull. soc. chim.* (4) **7**, 842–843 (1910). (12) Bock, Lock, Schmidt, *Monatsh*, **64**, 412 (1934). (13) Fuson, Corse, McKeever, *J. Am. Chem. Soc.* **62**, 3250 (1940). (14) Newman, *J. Am. Chem. Soc.* **59**, 2472 (1937). (15) Fuson, Denton, Kneisley, *J. Am. Chem. Soc.* **63**, 2652–2653 (1941). (16) Smith, Kiess, *J. Am. Chem. Soc.* **61**, 285–286 (1939). (17) Smith, Kiess, *J. Am. Chem. Soc.* **61**, 995–996 (1939). (18) Fuson, Ullyott, Hickson, *J. Am. Chem. Soc.* **61** 410–411 (1939). (19) Fuson, Denton, *J. Am. Chem. Soc.* **63**, 654–656 (1941).

1932, II 2371. (15) Bertozzi, *Gazz. chim. ital.* 29, II 37–38 (1899).

3:0410 2,6-DICHLOROBENZYL CHLORIDE $C_7H_5Cl_3$ Beil. S.N. 466



M.P. 39–40° (1)

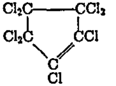
Colorless cryst. from lgr., ether, or alc. + ether.

[For prepn. of $\bar{C}$ from 2,6-dichlorotoluene (3:6270) by treatment at b.p. with Cl_2 in u.v. light see (1).]

$\bar{C}$ with Mg in dry ether gives 90% yield 2,6-dichlorobenzyl MgCl; this prod. upon treatment with CO_2 (1) or with methyl chloroformate (3:5075) followed by appropriate treatment yields 2,6-dichlorophenylacetic acid, cryst. from alc., m.p. 157–158° (1).

3:0410 (1) Austin, Johnson, *J. Am. Chem. Soc.* 54, 658–659 (1932).

3:0422 OCTACHLOROCYCLOPENTENE C_5Cl_8 Beil. V - 62
V₁—
V₂—



M.P.		B.P.				
41°	**(1) (8)**	**283–284°**	**at 733 mm.**	**(5) (6)**	D_4^{50} = **1.817 (4)**	n_D^{50} = **1.5660 (4)**
40–41°	**(7)**	**283°**		**(1)**		
40°	**(2)**	**183°**	**at 20 mm.**	**(2)**		
39°	**(3)**	**140°**	**at 10 mm.**	**(4)**		
38°	**(4)**					
32°	**(10)**					

[*See also hexachlorobutadiene*-1,3 (3:6425).]

Colorless cryst. from 95% alc. (4) or EtOH contg. 5% tetrachloroethylene (3:5460) (3).

[For prepn. of $\bar{C}$ from pentachlorocyclopentenone [Beil. VII-49] (7), from either the higher- or lower-melting stereoisomer of hexachlorocyclopentenone [Beil. VII-49] (1), from dibromo-dichloro-cyclopentanetrione [Beil. VII-853] (8), or from xanthogallol (tetrabromocyclopentenedione [Beil. VII₁-(321)] (2), all with PCl_5 in s.t., at elevated temps. as directed, see indic. refs.]

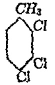
[For formn. from nonachloropentene-1 (itself obtd. from hexachloropropene (3:6370) with trichloroethylene (3:5170) + $AlCl_3$ (9)) by elimination of 1 HCl with alc. KOH yielding octachloropentadiene-1,3 followed by rearr. to $\bar{C}$ by boilg. with $AlCl_3$ see (3).]

[For formn. of $\bar{C}$ (together with CCl_4 (3:5100) and hexachloroethane (3:4835) by high-press./high-temp. chlorination of chloropentanes see (4); by exhaustive chlorination of hexyl iodide, heptaldehyde, heptylic acid, etc. (5), of high-mol.-wt. hydrocarbons (6), or of 3-chloro-5,6-dihydroxy-2-(dichloromethyl)pyridine [Beil. XII-164] (10), see indic. refs.]

Note that $\bar{C}$, formerly regarded as hexachlorobutadiene-1,3 (3:6425), is currently (3) believed to have the structure octachlorocyclopentene; for Raman spectra evidence see (11).

3:0422 (1) Zincke, Küster, *Ber.* **23**, 2214-2215 (1890). (2) Hantzsch, Strasser, *Ann.* **488**, 209 [illegible] 1791 (1941). (4) McBee, Hass, Pierson, *Ind Eng. Chem.* [illegible] 803-806 (1877). (6) Hartmann, *Ber.* **24**, 1011-1026 [illegible], *Ann.* **352**, 52-53 (1907). (9) [illegible] (10) Hoffmann, *Ber.* **22**, 1269-

3:0425 2,3,4-TRICHLOROTOLUENE $C_7H_5Cl_3$ ***Beil. V - 298***
V_1—
V_2-(232)



M.P. 41° (1) (2) (3) **B.P. 231-232° at 716 mm.** (1)
40-41° (4)

Ndls. from MeOH or EtOH; volatile with steam.

[For prepn. of C̄ from 2,3-dichloro-4-aminotoluene [Beil. XII-990] via diazotization and use of Cu_2Cl_2 reaction see (4); from toluene with $AlCl_3$ + SO_2Cl_2 (34% C̄ + 40% 2,4,5-trichlorotoluene (3:2100)) see (2); for formn. of C̄ (together with other isomers) from toluene, *o*-chlorotoluene (3:8245), or *p*-chlorotoluene (3 8287) with Cl_2 see (1), from 2,3-dichlorotoluene (3:6345) or 2,4-dichlorotoluene (3:6290) with Cl_2 in pres. of Al/Hg see (5); for prepn. of C̄ from its sulfonic acid by hydrolysis see (1) (7).]

[C̄ with Cl_2 in pres of Al/Hg yields (6) 2,3,4,6-tetrachlorotoluene (3:2480).]

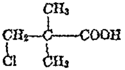
C̄ on mononitration (1) (4) by soln in cold fumg HNO_3 yields a mononitro C̄ [Beil. V-333], ndls from alc., m p. 60-61° (4), 60° (1); C̄ on dinitration by warming with a mixt. of 2 pts. fumg. HNO_3 and 1 pt. conc. H_2SO_4 (1) (4) cf. (7) yields 2,3,4-trichloro-5,6-dinitrotoluene [Beil. V-345], ndls. from alc., m.p. 141° (1) (2), 140-141° (4).

C̄ on shaking with 2 pts. fumg. H_2SO_4 at 60° yields (1) (7) a monosulfonic acid (use in sepn. of C̄ from 2,4,5-trichlorotoluene (3:2100) which is not sulfonated under these conditions (1) (7)).

C̄ on oxidn. with dil. HNO_3 in s.t. at 150° (4) yields 2,3,4-trichlorobenzoic acid (3:4810), m.p. 186-187° (4).

3:0425 (1) Seelig, *Ann.* **237**, 132, 137, 138, 140, 156 (1887). (2) Silberrad, *J. Chem. Soc.* **127**, 2681-2682 (1925). (3) I G., Brit 287,178, May 9, 1928, *Cent* **1929**, II 352. (4) Cohen, Dakin, *J. Chem. Soc.* **81**, 1327-1328 (1902). (5) Ref. 4, pp. 1339-1341. (6) Cohen, Dakin, *J. Chem. Soc.* **85**, 1283 (1904). (7) Prentzell, *Ann.* **296**, 181-182 (1897).

3:0440 CHLOROPIVALIC ACID $C_5H_9O_2Cl$ **Beil. S.N. 162**
(*β*-Chloro-*α*,*α*-
dimethylpropionic acid)



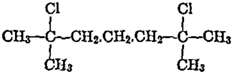
M.P. 40-42° (1) **B.P. 126-129° at 30 mm.** (1)

[For prepn. of C̄ from pivalic acid (trimethylacetic acid) (1:0410) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 see (1).]

Ⓓ **Chloropivalamide:** pl. from aq., m.p. 108-109° (1).

3:0440 (1) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925-929 (1940). (2) Kharasch, Brown (to du Pont Co.), U.S. 2,302,228, Nov. 17, 1942; *C.A.* **37**, 2018 (1943).

3:0455 2,6-DICHLORO-2,6-DIMETHYLHEPTANE $C_9H_{18}Cl_2$ **Beil. I - 167**
I_1—
I_2-(129)



M.P. 41–42° (1)

[For prepn. of C̄ from 2,6-dimethylheptanediol-2,6 [Beil. I-494] (2) with conc. HCl or AcCl see (1) (2); from the corresponding internal ether, viz., $\alpha,\alpha,\alpha',\alpha'$-tetramethylpentamethylene oxide (2,2,6,6-tetramethyltetrahydropyran) [Beil. XVII-17], with HCl see (1).]

C̄ on warming with aq. readily hydrolyzes (1) back to 2,6-dimethylheptanediol-2,6 (monohydrate, cryst. from C_6H_6, m p. 60–61°; anhydrous form by heating monohydrate at 135–140°, m.p. 76–77° (1).

[C̄ in C_6H_6 + AcOH treated with Zn dust in a stream of dry HCl yields (2) mixt. of α- and β-cyclogeraniols [Beil. VI-66, VI_1-(43)].]

3:0455 (1) Bruylants, *Bull. acad. roy. Belg.* **1909**, 276–282; *Cent.* **1909**, II 797; *C.A.* **4**, 1485 (1910); *Rec. trav. chim.* **29**, 130–133 (1910). (2) Staudinger, Widmer, *Helv. Chim. Acta* **9**, 531, 546–547 (1926).

3:0460 β-CHLOROPROPIONIC ACID $C_3H_5O_2Cl$ **Beil. II - 249**
(3-Chloropropanoic acid) $ClCH_2.CH_2.COOH$ II_1-(111)
II_2-(226)

M.P.	**42°**	(1) (2)	**B.P.**	**204°**	(11)
	41.5°	(3)		**203–205°** at 764 mm.	(12)
	41°	(4) (19)		**127°** at 35 mm.	(13)
	40.5° cor.	(5)		**120°** at 30 mm.	(27)
	40°	(6) (7)		**124°** at 25 mm.	(1)
	39°	(8) (9)		**105–107°** at 20 mm.	(14)
	38.5–39.5°	(10)		**108°** at 12 mm.	(1)

Lfts. from lgr or pet. eth — Very eas. sol. aq., alc., $CHCl_3$; spar. sol. dry ether. — Fairly hygroscopic. — C̄ on boilg. slightly dec. to HCl + acrylic ac. (1:1020). [Note that samples with m.p. higher than 42° may have contd. adipic ac. (8).] [For stability of C̄ in aq. soln. see (8).]

[For prepn. of C̄ from acrolein (1:0115) via addn. of HCl to β-chloropropionaldehyde (3:5576) and subsequent oxidn. with fumg. HNO_3 (yield: 65–70% (14), 60–65% (15), 50% (1)) see (15) (14) (7) (1) (16); from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) by oxidn. with conc. HNO_3 (yield: 78–79% (9)) (17) (13) (27) or alk. $KMnO_4$ (18) see indic. refs.; from β-hydroxypropionitrile (ethylene cyanohydrin) by hydrolysis with HCl see (10); from phosgene + ethylene + $AlCl_3$ via hydrolysis of intermediate β-chloropropionyl chloride (3:5690) see (19); for other methods see Beil. II-249.]

C̄ on htg. with aq. alk. or alk. carbonates (1) (7) (19) or on passing over activated carbon at 230–240° at 250–320 mm. (21) loses HCl and yields acrylic ac. (1:1020). [The alk. salts of C̄ dec. even at ord. temp. giving alk. chlorides (3).] [For example of use of C̄ as source of acrylic acid in Diels-Alder addn. reactions see under 9,10-dichloroanthracene (3:4916).]

C̄ with PCl_3 (12) or $SOCl_2$ (22) yields β-chloropropionyl chloride (3:5690) q.v., b p. 144°.

C̄ (1 g.) + pyridine (2 g.) htd. at 100° solidifies after 2 hrs. to give 100% yield addn. cpd. $\bar{C}.C_5H_5N$, pr. from abs. alc., m p. 160° (26).

—— Methyl β-chloropropionate: b.p. 148–150° at 760 mm. (3:5765)

—— Ethyl β-chloropropionate: b.p. 162–163° at 760 mm. (3:8290).

—— β-Chloropropionamide: unrecorded.

Ⓓ β-Chloropropionanilide: cryst. from aq. or MeOH, m.p. 119° (23). [From β-chloropropionyl chloride + aniline in acetone in 90% yield (23).]

Ⓓ β-Chloropropion-*p*-toluidide: cryst. from MeOH, m.p 121° (23) (22).

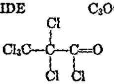
Ⓓ β-Phenoxypropionic acid: ndls. from hot aq. (24) or lgr. (25); m.p. 98° (24), 97–98° (25). [From C̄ + phenol + NaOH, 36% yield (25).]

3:0460 (1) Moureu, Murat, Tampier, *Ann. chim.* (9) **15**, 222–228 (1921). (2) Wooten, Hammett, *J. Am. Chem. Soc.* **57**, 2291 (1935). (3) Beckurts, Otto, *Ber.* **18**, 226, 846 (Note) (1885). (4) Michael, *Ber.* **34**, 4047–4048 (1901). (5) Linnemann, *Ann.* **163**, 96 (1872). (6) Lichty, *Ann.* **319**, 369–370 (1901). (7) Moureu, *Ann. chim* (7) **2**, 157–158 (1894); *Bull. soc. chim.* (3) **9**, 388 (1893). (8) Simpson, *J. Am Chem. Soc.* **40**, 675 (1918). (9) Powell, Huntress, Hershberg, *Org. Syntheses*, Coll. Vol. 1 (2nd ed), 168–169 (1941). (10) Jacobs, Heidelberger, *J. Am. Chem. Soc.* **39**, 1465–1466 (1917).

(11) de Barr, *Am Chem J.* **22**, 334 (1899). (12) Henry, *Compt. rend.* **100**, 114 (1885); *J. prakt. Chem.* (2) **31**, 126 (1885). (13) Powell, *J. Am. Chem. Soc.* **46**, 2879 (1924). (14) Moureu, Chaux, *Bull. soc. chim.* (4) **35**, 1360–1364 (1924). (15) Moureu, Chaux, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 166–168 (1941). (16) Arndt, *Ber.* **56**, 1276–1277 (Note) (1923). (17) Rojahn, *Ber.* **54**, 3116–3117 (1921). (18) Brit. (to I.G.), 479,690, Mar. 10, 1938; *Cent.* **1938**, I 3833; French 824,489, Feb 9, 1938; *C.A* **32**, 5857 (1938). (19) Pace, *Gazz. chim. ital* **59**, 580–582 (1929). (20) Klebanskii, Chevychalova, *Cent.* **1938**, I 1335, *C.A.* **34**, 6222 (1940).

(21) Bauer, Lauth (to Rohm and Haas Co.), U.S. 2,087,466, July 20, 1937; Ger. 646,820, June 23, 1937; *Cent.* **1937**, II 2072, Brit. 526,122, Sept. 11, 1940, *C.A.* **35**, 6981 (1941). (22) Wolffenstein, Rolle, *Ber* **41**, 736 (1908). (23) Mayer, van Zütphen, Philipps, *Ber.* **58**, 860 (1927); Mayer, Ger. 415,096, June 13, 1925, *Cent* **1925**, II 1094. (24) Powell, *J. Am. Chem. Soc.* **45**, 2710 (1923). (25) Arndt, Källner, *Ber.* **57**, 204 (1924). (26) Kirpal, Wojnar, *Ber.* **71**, 1264 (1938). (27) Fieser, Seligman, *J. Am Chem. Soc* **58**, 2484 (1936).

3:0470 PENTACHLOROPROPIONYL CHLORIDE C_3OCl_6 Beil. II — II_1-(112) II_2—



M.P. 42° (1)

Colorless not especially hygroscopic ndls.

[For prepn. of C̄ from trichloroacrylic acid chloride (3:5845) by addn. of Cl_2 in bright sunlight see (1).]

C̄ with $AlCl_3$ (1 mole) at 60° decomposes in two ways (1), leading on one hand to CO and hexachlorethane (3:4835), and on the other to phosgene (3:5000) and tetrachloroethylene (3:5460).

[C̄ with C_6H_6 + $AlCl_3$ yields (1) phenyl pentachloroethyl ketone (α,α,β,β,β-pentachloropropiophenone) [Beil. VII_1-(161)], m.p. 83° (1).]

C̄ on hydrolysis yields pentachloropropionic acid (3:4895).

3:0470 (1) Böeseken, Hasselbach, *Rec. trav. chim.* **32**, 11–13 (1913).

3:0475 *p*-CHLOROPHENOL  C_6H_5OCl Beil. VI - 186
VI$_1$-(100)
VI$_2$-(174)

M.P.		B.P.		
43°	(1)	219.75° at 760 mm.	(11)	$D_4^{78.1} = 1.2238$ (22)
42.9°	(2) (3)	218.3–218.9°	(12)	$n_D^{65} = 1.5480$ (23)
42.5°	(4)	218°	(6) (15)	$n_D^{40} = 1.5600$ (14)
40–41°	(5)	217° at 760 mm.	(7)	1.5579 (3)
41°	(6) (15)	217°	(10)	$n_D^{20} = 1.5690$ (14)
40°	(7)	216.0° at 760 mm.	(13)	
38–39°	(8)	99.7° at 12 mm.	(13)	
37°	(9) (10) (20) (55)			
36°	(39)			

[*See also o-chlorophenol* (3:5980).]

$\bar{C}$ has disagreeable and persistent odor (15) for study of strength of which in aq. soln. see (16). — $\bar{C}$ is spar. sol. aq. at ord. temp. (for details see (17)); but $\bar{C}$ is eas. sol. alc., ether, C_6H_6, $CHCl_3$, CS_2. — $\bar{C}$ (like its *o*-isomer (3:5980)) is volatile with steam (for studies see (18)) even from soln. in equiv. aq. NaOH (19) (dif. and sepn. from 2,4-dichlorophenol (3:0560), 2,6-dichlorophenol (3:1595), and 2,4,6-trichlorophenol (3:1673) (19).

The cryoscopic const. of $\bar{C}$ is 85.8 (20).

SELECTED DATA ON BINARY SYSTEMS CONTG. $\bar{C}$

$\bar{C}$ + aq.: for solubility/temp. data see (17).

$\bar{C}$ + C_6H_6: for solubility/temp. data (17) or for vapor-press. data (21) see indic. refs.; for association of $\bar{C}$ in C_6H_6 soln. see (30). **$\bar{C}$ + MeOH (1:6120):** for vapor-press. data see (21). **$\bar{C}$ + acetone (1:5400):** for vapor-press. data see (21). **$\bar{C}$ + methyl acetate (1:3005):** for vapor-press. data see (21).

$\bar{C}$ + nitrobenzene: for f.p./compn. data and diagrams see (24) (25), eutectic m.p. −24.5° contg. 41.5 wt. % $\bar{C}$ (24), m.p. −30.5° contg. 50.5 mol. % $\bar{C}$ (25).

$\bar{C}$ + aniline: for D_{-}^{25} and D_{-}^{50} + viscosity at 25° and 50° see (26). **$\bar{C}$ + *p*-toluidine:** for f.p./compn. and n_D^{54}/compn. data and diagrams see (4) cf. (29); note two eutectics, E_1, m.p. 21° contg. 28 mol. % $\bar{C}$, and E_2, m.p. 7.4° contg. 71 mol. % $\bar{C}$ (4). **$\bar{C}$ + benzylamine:** for f.p./compn. diagram see (27), noting two molecular cpds., one of compn. 3 $\bar{C}$.1 benzylamine, m.p. 55°, the other 1 $\bar{C}$.1 benzylamine, m.p. 16° (27). **$\bar{C}$ + phenylhydrazine:** for f.p./compn. data and diagram see (1).

$\bar{C}$ + piperidine: for n_D^{65}/compn. data see (23).

$\bar{C}$ + pyridine: for f.p./compn. diag. of entire system see (4) cf. (28) (note two eutectics, viz., E_1, m.p. −19.5° contg 66.6 mol. % $\bar{C}$, E_2, m.p. −47.3° contg. 13.5 mol. % $\bar{C}$); for n_D^{25}/compn. and n_D^{50}/compn. data over entire system see (14).

$\bar{C}$ + *o*-chlorophenol (3:5980): for f.p./compn. data and diagram see (3) (note that the eutectic, m.p. about −20.5°, conts. about 38.5 mol. % $\bar{C}$). **$\bar{C}$ + *p*-dichlorobenzene (3:0980):** for f.p./compn. diagram see (4) (note eutectic m.p. 27.2° contg. 73.4 mol. % $\bar{C}$); for n_D^{54}/compn. data see (4).

Azeotropic Systems Contg. $\bar{C}$

$\bar{C}$ with naphthalene (1:7200) forms a const.-boilg. mixt., b.p. 216.3° contg. 36.5% $\bar{C}$ (11). $\bar{C}$ with *p*-dibromobenzene forms a const.-boilg. mixt, b.p. 215.05° contg. 35% $\bar{C}$ (11).

PREPARATION OF $\bar{C}$

From *p*-chloroaniline. [For prepn. of $\bar{C}$ from *p*-chloroaniline (Beil. XII-607, XII_1-(304)] via diazotization to salts of *p*-chlorobenzenediazonium hydroxide (Beil. XVI-463, XVI_1-(355)] and hydrolysis of the latter (yields not stated) (3) (10) in an inert solvent (31) see indic. refs.; for study of rate of hydrolysis (32) of *p*-chlorobenzenediazonium chloride and influence of light thereon (33) see indic. refs.]

From phenol. [For prepn. of $\bar{C}$ from phenol (1:1420) with Cl_2 at temps. over range 40°–155° see (3) cf. (6) (35); with Cl_2 + conc. aq. Na_2CO_3 soln. see (34), by use of *N,N*-dichlorobenzenesulfonamide in $CHCl_3$ at −15° see (36) (note that evidence obtd. from this reaction in pres. of isobutylene indicates that phenyl hypochlorite is first formed and subsequently rearranges (36)); by use of *N,N'*-dichlorourea + HCl see (37), with EtOCl (3:7022) in CCl_4 at −20° see (38); or by use of SO_2Cl_2 see (39) (40) (41) (for use of SO_2Cl_2 on $NaOC_6H_5$ see (7)). — Note that in all these methods some *o*-chlorophenol (3:5980) is usually also formed.]

From *p*-aminophenol. [For formn. of $\bar{C}$ from *p*-aminophenol (Beil XIII-427, $XIII_1$-(143)] via diazotization, conversion to corresp $PtCl_4$ double salt, and dry distn. see (42); or via diazotization, conv. to corresp. $ZnCl_2$ double salt, and decompn. by addn of molten phenol (yield 40% accompanied by 41% hydroxybiphenyl + 11% diphenyl ether) see (43).]

From *p*-dichlorobenzene. [For prepn. of $\bar{C}$ from *p*-dichlorobenzene (3:0980) with MeOH/NaOMe in s.t. at 180° (44) (45), or with MeOH/NaOH in s.t. at 190–195° (90% yield (46)) or at 200° for 25 hrs. under press. (8), see indic. refs.; for use of aq. alk. or alk. earths with MeOH in pres of copper salts at 150–190° under press see (47) (note, however, that, although the hydrolysis of *p*-dichlorobenzene to $\bar{C}$ is markedly facilitated by presence of Cu, e.g., with aq. NaOH, maximum yield is 30% while with MeOH/NaOH + Cu yield is 85% (48), yet in presence of Cu_2O some ord. phenol (1:1420) is also formed (49); for prepn. of $\bar{C}$ from *p*-dichlorobenzene (3 0980) by vapor-phase hydrolysis with steam + cat. at 550–850° see (50).]

From other miscellaneous sources. [For formn of $\bar{C}$ from various *p*-chlorophenyl ethers by cleavage, e.g., from *p*-chloroanisole (3:6300) with conc. HCl in s.t. (51) or with MeOH/NaOMe in s.t. at 176° (45); from *p*-chlorophenetole (3.0090) with conc. HCl (52) or with HBr in AcOH (85% yield (53)); or from *p*-chlorophenoxyacetic acid (3:4375) with conc. HCl in s.t. at 150° (34), see indic. refs]

[$\bar{C}$ is also obtainable by hydrolysis of its various esters, but these need not be cited here.]

[For formn. of $\bar{C}$ from *p*-bromophenol with SO_2Cl_2 at ord temp see (55); from calcium salt of *p*-dichlorobenzenesulfonic acid with $Ca(OH)_2$ + Cu at 200–220° followed by removal of the sulfonic acid group from the resultant *p*-chlorophenolsulfonic acid see (56)]

BIOCHEMICAL ASPECTS OF $\bar{C}$

[For studies involving fate of $\bar{C}$ in animal metabolism see (57) (58) (59); for studies from various aspects of bactericidal and fungicidal action of $\bar{C}$ see (60) (61) (62) (63) (64) (65) (67) (68).]

[For studies from various aspects of effect of $\bar{C}$ and other chlorophenols on taste of water see (69) (70) (71) (72) (73).]

MISCELLANEOUS USES OF $\bar{C}$

[For use of $\bar{C}$ in selective solv. refining of mineral oils see (74); as denaturant for alc. see (75); as solv. for lignin see (76).]

QUANT. DETN. OF C̄

See text below under bromination of C̄, iodination of C̄, and nitration of C̄.

CHEMICAL BEHAVIOR OF C̄

PYROLYSIS OF C̄

[C̄ on pyrolysis through silica tube at red heat gives (77) 3,6-dichlorodiphenylene oxide, m.p. 188° (77).]

REDUCTION OF C̄

[C̄ with H_2 + Ni cat. in aq. or aq. alc. alk. soln. loses chlorine quant. as HCl (78) (for study of rate see (79)); note also that C̄ with Li at 220° (80) or with Ca at 160° (80) followed by treatment with aq. gives (yields 14% and 36% resp.) phenol (1:1420). — Note that C̄ with aq. Cu_2O at 250–380° under press. gives (81) phenol (1:1420) (see also above under prepn. of C̄ from p-dichlorobenzene). — Note that reduction of C̄ to 4-chlorocyclohexanol-1 (3:9376) appears to be unreported.]

OXIDATION OF C̄

[C̄ on oxidn. with 35% peracetic acid at 25° gives (82) slowly (17 days) in small yield β-chloromuconic acid (2-chlorobutadien-1,3-dicarboxylic acid-1,4), m.p. 223°, accompanied in the mother liquor by some lactone ($C_6H_5O_5Cl$) of 3-chloro-4,5-dihydroxyhexen-2-dioic acid-1,6, m p. 177° (82). — C̄ on electrolytic oxidn. gives (83) benzoquinone-1,4 (1:9025).]

NUCLEAR SUBSTITUTION OF C̄

(See also below under condensation reactions of C̄.)

Halogenation of C̄. *Fluorination.* [The fluorination of C̄ has not been reported, and no fluoro- or difluoroderiv. of C̄ is known.]

Chlorination. [C̄ with Cl_2 (2 moles) in AcOH in cold gives (80% yield (84)) 2,4-dichorophenol (3:0560), m.p. 45°; presumably C̄ with Cl_2 (3 moles) would give 2,4,6-trichlorophenol (3:1673), but such reaction is not actually reported. — For study of rate of chlorination of C̄ with Cl_2 in CCl_4 (85) or with NaOCl in alk. soln. at 25° (86), or behavior of C̄ with Cl_2 in presence of radioactive HCl in C_6H_6 soln. (87), see indic. refs.]

Bromination. [C̄ with Br_2 (1 mole) in CCl_4 at room temp. gives (62% yield (88)) 2-bromo-4-chlorophenol, m.p 33–34°, b.p. 121–123° at 10 mm. (corresp. benzoyl deriv., m.p. 99–100°) (88).]

C̄ with Br_2 (2 moles) in AcOH (89) (90) (91) or C̄ with Br_2 (2 moles) in aq. KBr soln. (92) gives (yields not stated) 4-chloro-2,6-dibromophenol, ndls. from dil. alc., m.p. 92° (89), 90° cor. (92), 89° (90) (corresp. methyl ether, m.p. 74° (92); 2,4-dinitrophenyl ether, m.p. 145–146° (90), p-toluenesulfonate, m.p. 107–108° (90)). [Note difference from the isomeric 4-chloro-3,5-dibromophenol, m.p. 121° (93), 118° (94) (corresp. Me ether, m.p. 82.5° (93), benzoyl deriv., m.p. 132° (94)).]

[C̄ with Br_2 (4 moles) in pres. of Fe powder gives (93) 4-chloro-2,3,5,6-tetrabromophenol, m.p. 215° (corresp. methyl ether, m.p. 161°, benzoyl deriv., m.p. 203° (93)).]

[For quant. detn. of C̄ by dibromination with $KBrO_3$/KBr soln. see (95) (96) (97).]

Iodination. C̄ with I_2 (1 mole) in aq. KI + conc. NH_4OH gives (88% yield (98)) 4-chloro-2-iodophenol, ndls. from $CHCl_3$ or lt. pet., m p. 78° (98) (99) (corresp. acetyl deriv., m p. 57° (98); corresp. benzoyl deriv., m.p. 88° (99), 83–84° (98); corresp. N-phenylcarbamate, m.p. 128° (99)).

C̄ with excess I_2 in aq. KI + conc. NH_4OH (98), or C̄ in alk. soln. with I_2 in aq. KI (92),

or C̃ in alk. soln. with $I_2 + KIO_3$ followed by dil H_2SO_4 (89), or C̃ with ICl (99), gives (89% yield (98)) 4-chloro-2,6-iodophenol, ndls. from alc. or lt. pet., m.p. 109° cor. (92), 108° (93) (100), 107–108° (89), 106–107° (99) (corresp. methyl ether, m.p. 79° (92); corresp. acetyl deriv., m.p. 128° (98), 127.5° (100)).

{For quant. detn. of C̃ by di-iodination using I_2 + borax sol- [illegible]}

Nitration of C̃. C̃ on mononitration with [illegible] th 30% HNO_3 in cold (103), or with nitro[illegible] H with HNO_3 (105), gives [illegible] [Beil. VI-238, [illegible] (101) (102) (corresp. [illegible] corresp. ethyl ether, m.p. 61–62° (101); cor- [illegible] (99)). — {For use of mononitration in quant. detn. of m[illegible] o-chlorophenol (3:5980) see (107) cf. (112).}

C̃ on dinitration with conc. HNO_3 (108) (or the above 4-chloro-2-nitrophenol on further nitration with fumg. HNO_3 (101)) gives 4-chloro-2,6-dinitrophenol [Beil. VI-260, VI_1-(128)], yel. ndls. or lfts. from aq., ndls. or pr. from alc., ether, or $CHCl_3$, m.p. 81° (108) (corresp. methyl ether, m.p. 66° (109), 64° (94), corresp. ethyl ether, m.p. 54–55° (110); corresp. N-phenylcarbamate cannot be prepared (111)).

Nitrosation of C̃. {Unlike the isomeric o-chlorophenol (3:5980) the nitrosation of C̃ has not been reported, and no nitroso-p-chlorophenol is known.}

Sulfonation of C̃. {C̃ with equiv. amt. fumg H_2SO_4 (D = 1.90) at 100° (113) (114) gives 4-chlorophenolsulfonic acid-2 [Beil. XI-236], deliquescent tbls. of monohydrate from aq., m.p. 75–76° (113) (for study of acid strength see (115)) — Note also that C̃ with very large excess (15 wt. pts.) fumg H_2SO_4 (20% SO_3) gives (80–85% yield (116)) a bimolecular condensation prod. of the above sulfonic acid.}

Mercuration of C̃. {C̃ with $HgO/HgSO_4$ on warming, followed by neutraliz. with NaOH, gives (117) 4-chloro-2-hydroxymercuriphenol [Beil. XVI_1-(564)]. — For other studies of mono- and di-mercuration of C̃ see (118) (119); for patents see (120) (121).}

Condensation Reactions Involving Nuclear Hydrogen of C̃

With alcohols. C̃ with alcs. contg. more than one C in pres. of conc. $HClO_4$ at 0–160° gives ultimately (although doubtless through formn. of intermediate esters followed by rearr. or intermediate formn. of olefins followed by addn.) (122) the corresp. 2-alkyl-4-chlorophenols [e.g., C̃ with isopropyl alc. (1:6135) + conc. $HClO_4$ as directed (122) gives 4-chloro-2-isopropylphenol, sol. aq. NaOH, b.p. 235–250° accompanied by 4-chloro-2,6-diisopropylphenol, insol. aq. NaOH, m.p. 260–265°].

With aldehydes. {C̃ with formaldehyde (1:0145) + conc. HCl + H_2SO_4 is claimed (123) to undergo simple chloromethylation yielding 5-chloro-2-hydroxybenzyl chloride, m.p. 85° (123); note, however, that further condensation (involving 2 additional moles of formaldehyde) may occur giving (67% yield (124)) 6-chloro-8-(chloromethyl)benzodioxane-1,3, cryst. from MeOH, m.p. 103° (124). — C̃ with formaldehyde (1:0145) + aq. alkali gives (125) 4-chloro-2,6-bis-(hydroxymethyl)phenol ("p-chlorophenol dialcohol"), m.p. 154° (126) (corresp. mono-(p-toluenesulfonate), m.p. 151° (127)); note that reaction of C̃ with 1 mole formaldehyde to give 4-chloro-2-(hydroxymethyl)phenol (5-chlorosalicyl alcohol) is not reported although the latter [Beil. VI-893], m.p. 93°, is known.}

With $CHCl_3$, chloral, or hexamethylenetetramine. {C̃ with $CHCl_3$ + EtOH + aq. NaOH (128), or C̃ with hexamethylenetetramine in anhydrous glyceroboric acid at 150–155° followed by H_2SO_4 hydrolysis (129), or C̃ with chloral + anhydrous Na_2HPO_4 at 70–75° (giving (4-chloro-2-hydroxyphenyl)-trichloromethyl-carbinol cf. (130)) followed by hydrolysis + oxidation (131), gives (18% yield (129)) 5-chloro-2-hydroxybenzaldehyde (5-chlorosalicylaldehyde) (3:2800), m.p. 99–100°.}

With CCl_4. [C̄ with CCl_4 in aq. NaOH (128) in pres. of Cu or Cu compds. (132) or C̄ with CCl_4 in alc. KOH in s.t. at 140° for 5–6 hrs. (133) gives 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705), m.p. 172°.]

With CO_2 or organic acids. [C̄ (as dry NaĀ) with CO_2 at 140–150° under press. gives (135) (136) Na salt of 5-chlorosalicylic acid (3:4705) (see also above).]

[C̄ with *o*-chlorobenzoic acid (3:4150) in MeOH/NaOMe + trace Cu powder evapd., htd. at 200°, then htd. with conc. H_2SO_4 for 15 min. gives (136) 2-chloroxanthone, m.p. 165° (136).]

With acid chlorides of organic acids. The conventional type of reaction of C̄ with acyl halides is to form the corresp. *p*-chlorophenyl esters (see also below under reactions of phenolic hydrogen of C̄); however, with C̄ acid chlorides in pres. of $AlCl_3$ the ultimate product (undoubtedly formed by rearr. of an intermediate ester) is the ketone [e.g., C̄ with benzoyl chloride (3:6240) + $AlCl_3$ in CS_2 (137) or acetylene tetrachloride (3:5750) (138) gives 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p. 95.0–95.5° (138), 94–95° (139), 94° (137), 93–94° (140), frequently accompanied by *p*-chlorophenyl benzoate, m.p. 87° (see below); for analogous behavior of C̄ with *o*-toluyl chloride (3:8740) see (138)].

With anhydrides. [C̄ with phthalic anhydride (1:0725) + $AlCl_3$ at 140–145° (141) cf. (143) or in acetylene tetrachloride (3:5750) (142) gives (70% yield (142)) *o*-(5-chloro-2-hydroxybenzoyl)benzoic acid [Beil. X_1-(470)], cryst. from hot AcOH, acetone, or alc., m.p. 202°, after sintering at 192° (142); this product ring-closes under the conditions of its formn. (141) (142) (143) (144) or with conc. H_2SO_4 at 100° (144) (142) cf. (141) giving 4-chloro-1-hydroxyanthraquinone [Beil. VIII-340, $VIII_1$-(651)], yel.-or. ndls. from AcOH or pyridine, m.p. 194° (141), 193–194° (145), 192–193° (146), 189° (142), 188° (147) (corresp. methyl ether, m.p. 168° (145), corresp. acetate, m.p. 176–177° (146)), also obtd. (70% yield (145)) directly from C̄ with phthalic anhydride (1:0725) + $AlCl_3$ + NaCl at 200–220° for 3 hrs. (See also next paragraph.)]

[Note, however, that C̄ with phthalic anhydride (1:0725) + conc. H_2SO_4 at 200° (148) (149) or in pres. of conc. H_2SO_4 + H_3BO_3 at 200° for 3½ hrs. (150) (151) (143) (152) (153) (154) (155) (156) goes further than above giving (yield: 68–74% (150)) 1,4-dihydroxyanthraquinone (quinizarin) (1:9085), cryst. from AcOH, m.p. 200–202° cor. (150).]

[C̄ with 4-chlorophthalic anhydride (3:2725) + H_3BO_3 + fumg. H_2SO_4 at 175–195° for 20 hrs. gives (157) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), tbls. from toluene, m.p. 188° (158) (corresp. dimethyl ether, m.p. 168.5° (158); diacetate, m.p. 213° (158)). — *For completely analogous behavior under similar circumstances of C̄ with* 3,4-dichlorophthalic anhydride (3:3695) or C̄ with 4,5-dichlorophthalic anhydride (3:4830) see these cpds.]

[C̄ with 4-sulfophthalic anhydride + H_3BO_3 + H_2SO_4 at 200° for 4 hrs. gives (45% yield (159) (160) cf. (161)) 1,4-dihydroxyanthraquinonesulfonic acid-6 (6-sulfoquinizarin) [Beil. XI-357]; for study of Na salt of latter as acid-base indicator see (162).]

[For behavior of C̄ with 3-methylphthalic anhydride + $AlCl_3$ (144) (163), with 4-methylphthalic anhydride + $AlCl_3$ (163), with naphthalene-1,2-dicarboxylic acid anhydride + $AlCl_3$ + NaCl (164), or with naphthalene-2,3-dicarboxylic acid anhydride + $AlCl_3$ + NaCl (165), see indic. refs.]

With esters of keto acids. [C̄ (1 mole) with ethyl acetoacetate (1:1710) + conc. H_2SO_4 stood 24 hrs. gives (2.7% yield (166)) 6-chloro-2-methylcoumarin [Beil. XVII-336, $XVII_1$-(173)], m.p. 186–187° (167), 186° (168), 185° (170), 184–185° (166), 184° (169); note, however, that 4-chloro-2-acetylphenol (5-chloro-2-hydroxyacetophenone) (see below) with Ac_2O + NaOAc at 160–170° for 5 hrs. gives (167) *both* the above 6-chloro-2-methylcoumarin and the isomeric 6-chloro-2-methylchromone, ndls. from AcOH, m.p. 115–116° (167).]

[Note also that C̄ with *α*-alkylacetoacetates + P_2O_5 gives the corresp. chromones: e.g.,

$\bar{C}$ with ethyl α-methylacetoacetate (1:1712) gives (17% yield (171)) 6-chloro-2,3-dimethylchromone, m.p. 107°; $\bar{C}$ with ethyl α-ethylacetoacetate (1:1723) gives (171) 6-chloro-3-ethyl-2-methylchromone, m.p. 109°; $\bar{C}$ with ethyl α-(n-propyl)acetoacetate gives (172) 6-chloro-2-methyl-3-n-propylchromone, m.p. 108°; $\bar{C}$ with ethyl α-isopropylacetoacetate gives (172) 6-chloro-2-methyl-3-n-propylchromone, m.p. 108°; $\bar{C}$ with ethyl α-isopropylacetoacetate gives (172) 6-chloro-3-isopropyl-2-methylchromone, m.p. 127°.]

[$\bar{C}$ with diethyl oxaloacetate + conc. H_2SO_4 at 0° gives (small yield (170)) ethyl 6-chlorocoumarin-4-carboxylate [Beil. XVIII$_1$-(493)], yel. ndls., m.p. 96–97°; $\bar{C}$ with diethyl acetonedicarboxylate (1:1772) + conc. H_2SO_4 gives (6% yield (170)) ethyl 6-chlorocoumarinyl-4-acetate [Beil. XVIII$_1$-(493)], m.p. 167°.]

With diazonium salts. $\bar{C}$ in alk. soln. couples with diazonium salts giving upon acidification the corresp. chloro-hydroxy-azo derivs. [e.g., $\bar{C}$ with benzenediazonium chloride (aniline diazotized in HCl soln.) gives (173) 4-chloro-2-(benzeneazo)phenol (5-chloro-2-hydroxyazobenzene) [Beil. XVI-93], red-or. ndls. from AcOH, mp. 110–111° (173) (174); $\bar{C}$ with diazotized p-nitroaniline gives (175) 4-chloro-2-(p-nitrobenzeneazo)phenol, m.p. 140–143°; for patent on coupling of $\bar{C}$ with other diazonium salts see (176)].

With other miscellaneous reactants. [For condensation of $\bar{C}$ with indene (di)chloride (2,3-dichloroindane) see (177); for condensation of $\bar{C}$ with o-nitrobenzenesulfinic acid (178) or with 2-chloro-5-nitrobenzenesulfinic acid (179) see indic. refs.; for oxidative condensation of $\bar{C}$ with N,N-dialkyl-p-phenylenediamines, etc., to give various indophenols see (180).]

[$\bar{C}$ (2 moles) with SCl_2 (1 mole) in CCl_4 at −10° (181) or in CS_2 at 40–45° (70% yield (182)) or $\bar{C}$ with S_2Cl_2 in CS_2 at room temp. (42% yield (182)) gives bis-(5-chloro-2-hydroxyphenyl) sulfide [Beil. VI$_1$-(396)], ndls. or lfts. from C_6H_6, m.p. 175° (183), 174° (182), 173–174° (184), 173° (181) (corresp. dimethyl ether, m.p. 112° (182); diethyl ether, m.p. 145° (185), dibenzoate, m.p. 145° (182)); for use as disinfectant (181) (183) or in mothproofing compositions (186) see indic. refs.]

[$\bar{C}$ (2 moles) with $SOCl_2$ (1 mole) + $AlCl_3$ in CS_2 gives (70% yield (184)) bis-(5-chloro-2-hydroxyphenyl) sulfoxide [Beil. VI$_1$-(396)], pr. from dil. alc., m.p. 202° (corresp. dinitration prod., m.p. 180–181° (184)).]

Reactions Involving Nuclear Halogen of $\bar{C}$

[$\bar{C}$ on fusion with KOH (187) (188) or $\bar{C}$ with aq. alkali or alk. carbonates in pres. of Cu or Cu compds. at elevated temp under press. (189), or $\bar{C}$ with aq. $Ba(OH)_2$ at 170–195° under press. (190), or $\bar{C}$ with alkali or alk.-earth hydroxides + Cu salts at elevated temp. under press. (191) gives 1,4-dihydroxybenzene (hydroquinone) (1:1590); note, however, that in such fusions with alkali some 1,3-dihydroxybenzene (resorcinol) (1:1530) is also formed (187) (188) (192) (193), and $\bar{C}$ (as Na$\bar{A}$) with NaOH at 310° for 5 hrs. gives (194) as high as 38% resorcinol (1:1530) + a trace of 2,4'-dihydroxybiphenyl; however, $\bar{C}$ on fusion with K_2CO_3 is claimed (193) to yield only hydroquinone (1:1590).]

[$\bar{C}$ with Na_2S + NaOH at 210–215° for 24 hrs. gives (195) 4-mercaptophenol (monothiohydroquinone) [Beil. VI-859, VI$_1$-(419)], m.p. 29–30°.]

[$\bar{C}$ with NH_3 in pres. of Cu cpds. htd. under press. gives (196) p-aminophenol; $\bar{C}$ similarly with prim. aliphatic amines gives (196) corresp N-alkyl-p-aminophenols.]

Reactions of $\bar{C}$ Involving Phenolic H (i.e., H of the OH Group)

Acidic strength. $\bar{C}$ behaves as weak acid, is soluble in aq alk. or in large excess (2.75 moles of 2 N (197)) aq Na_2CO_3 soln. from which it is repptd by CO_2 (197). — Dissoc. const. of $\bar{C}$ in aq. at 28.5° = 6.6×10^{-10} (198); for studies of dissoc. const. in other solutions, e.g., in 50% MeOH at 20° (199) (200) or at 28.5° (198), or at 18° over range 0–95% MeOH by volume (203), in 30% aq. EtOH at 25° (200) (9) (201), or at 18° over range

0–95% EtOH by vol. (202), see indic. refs. — For hydrogen potential of C̄ in 48.95 vol. % EtOH or 95 vol. % EtOH at 20° see (204). — For titration of C̄ with standard NaOH and indicator see (205).

Salts of C̄. [NaĀ; from C̄ in abs. EtOH with equiv. Na, evapd. under H_2, dried at 140–150° (134); very hygroscopic ndls. from conc. alc. soln., turning brown in air; in contrast to Na phenolate is fairly eas. sol. dry ether (206); for behavior with CO_2 at 140–150° giving Na salt of 5-chlorosalicylic acid (3:4705) see (134) (135).]

[C̄ (38.4 pts.) with KOH (5.6 pts.) in C_6H_6 gives (207) KĀ.2C̄.]

[C̄ with $AlCl_3$ evolves heat and HCl giving (208) $Cl.C_6H_4.OAlCl_2$, m.p. 185–187° (208).]

[For patents on use of alkali salts of C̄ as anti-gumming agents for motor fuels see (209); for use of aq. solns. of salts of C̄ as wash liquid for fuel gas purification see (210).]

Etherification (see also below under Ⓓ's)

Aliphatic ethers of C̄. C̄ with alkyl halides usually in presence of an acid acceptor gives the corresponding *p*-chlorophenyl ethers [e g., for *methyl ether* (*p*-chloroanisole) (3:6300) or for *ethyl ether* (*p*-chlorophenetole) (3:0090) see these compds. — *p-Chlorophenyl n-propyl ether* appears to be unreported; for *p-chlorophenyl isopropyl ether*, b.p. 101° at 17 mm. (211), 73–75° at 1.5 mm. (212), n_D^{25} = 1.5127 (212), see indic. refs. — For *p-chlorophenyl isobutyl ether*, b.p. 95–97° at 3 mm., n_D^{25} = 1.5090, see (213); the *n-butyl*, *sec-butyl* and *ter-butyl ethers* are unreported. — For *p-chlorophenyl n-amyl ether*, b.p. 132–133° at 12 mm., *p-chlorophenyl n-hexyl ether*, b.p. 172° at 34 mm., *p-chlorophenyl n-heptyl ether*, b.p. 162° at 14 mm., and *p-chlorophenyl n-hexadecyl ether*, m.p. 48°, see (214)].

[C̄ with vinyl chloride (3:7010) + aq. NaOH + $CuCl_2$ at 170–190° for 10 hrs. under press. gives (215) *p*-chlorophenyl vinyl ether, b.p. 193–194°, D_{-}^{20} = 1.138. — C̄ with allyl bromide + K_2CO_3 in acetone gives (100% yield (216)) *p*-chlorophenyl allyl ether, b.p. 232–234° at ord. press., 106–107° at 12 mm.; note that distn. at ord. press. causes thermal rearr. to 4-chloro-2-allylphenol, b p. 137° at 18 mm., 124–125° at 12 mm., m.p. 48° (corresp. *p*-nitrobenzoate, m.p. 82°) (216). — C̄ with methallyl chloride (3:7145) + K_2CO_3 in acetone gives (217) *p*-chlorophenyl methylallyl ether, b.p. 101.5° at 8 mm., D_{20}^{20} = 1.0979, n_D^{20} = 1.5304; this prod. on thermal rearr. gives (217) 4-chloro-2-methallylphenol, b p. 113° at 8 mm., D_{20}^{20} = 1.145, n_D^{20} = 1.5622, accompanied by some 5-chloro-2,2-dimethylcoumaran, b.p. 96° at 5 mm., D_{20}^{20} = 1.135, n_D^{20} = 1.5300 (217).]

[C̄ with ethylene oxide (1:6105) in alc. NaOEt adds giving (218) cf. (219) ethylene glycol mono-(*p*-chlorophenyl) ether (*p*-chlorophenyl β-hydroxyethyl ether), m.p. about 28° (corresp. *p*-nitrobenzoate, m.p. 90–91°) (218); note that the corresp. ethylene glycol *bis*-(*p*-chlorophenyl ether) is unreported.]

[C̄ (as NaĀ) with 2-chloropropanol-1 (3:7917) gives (220) *p*-chlorophenyl β-hydroxyisopropyl ether (propylene glycol β-(*p*-chlorophenyl) ether), b.p. 151–153° at 18 mm. — C̄ with 3-chloropropanediol-1,2 (glycerol α-monochlorohydrin) (3:9038) *in alk. soln.* (221), or C̄ with glycerol (1:6540) + NaOAc at 200–210° in atmosphere of illuminating gas (222) gives *p*-chlorophenyl β,γ-dihydroxy-*n*-propyl ether (glycerol α-(*p*-chlorophenyl ether), cryst. from C_6H_6, m.p. 80° (221), 76° (222); b.p. 214–215° at 19 mm. (221), 173–175° at 17 mm. (223).]

[C̄ with diethyl chlorofumarate (3:6864) + NaOEt at 150° gives (224) diethyl *p*-chlorophenoxyfumarate, b.p. 199–200° at 12 mm. — C̄ (as NaĀ) + C̄ with ethyl phenylpropiolate as directed gives (224) ethyl β-(*p*-chlorophenoxy)cinnamate, m.p. 63–64°, b.p. 220–225° at 12 mm]

Aromatic ethers of C̄. [illegible] at 19 mm. (225), 146–150° at 7 mm. (226), [illegible] prod. has not been reported by etherification [illegible] (1:7125) in AcOH

with Cl_2 (226), from K phenolate + p-chloroiodobenzene (225), or from p-aminophenol *phenyl ether via diazotization and use of Cu_2Cl_2 reaction (226); for studies of its chlorination*, bromination, iodination, and nitration see (226), for metalation see (227); note also that the product first reported (228) was impure (225).]

p-Chlorophenyl p-chlorophenyl ether (*bis-(p-chlorophenyl) ether*) [m.p. 30° (226) (229), b.p. 168–172° at 7 mm (226); note that this prod has not been reported by etherification of C̄ but has been prepd. from diphenyl ether (1:7125) in AcOH with Cl_2 (226), or from *p*-aminophenol *p*-chlorophenyl ether via diazotization and use of Cu_2Cl_2 reaction (226) (229); for mononitration to 4-chlorophenyl 4-chloro-2-nitrophenyl ether, m.p. 75° (see also below) or dinitration to *bis*-(4-chloro-2-nitrophenyl) ether, m.p. 152° (229), 154° (230), see (229) (230)]

p-Chlorophenyl o-nitrophenyl ether [from C̄ (as KĀ) with *o*-chloronitrobenzene on htg (230) (231) in pres. of Cu bronze (232) (yields· 75% (232), 72% (230)), pale yel. cryst. from MeOH, m.p. 46° (231), 45.5° (230), 44–45° (232), b.p. 220° at 20 mm. (232), 208° at 11 mm. (232); note that this prod does *not* (229) react with piperidine at 100°]

p-Chlorophenyl m-nitrophenyl ether [m.p. 60° (233), reported only by indirect means (233)].

p-Chlorophenyl p-nitrophenyl ether: from C̄ (as KĀ) with *p*-chloronitrobenzene on htg (81% yield (230)) (229) (233), m.p. 76.6° (230), 76° (233), 75.5–76° (229); b.p. 215° at 12 mm. (229) or as one prod of nitration of *p*-chlorophenyl phenyl ether (above) (226) — [For pat. on use as insecticide see (134).]

p-Chlorophenyl 2,4-dinitrophenyl ether: from C̄ (as KĀ (230) or NaĀ (235)) with 2,4-dinitrochlorobenzene on htg (97% yield (230)); yel. tbls. from 1:2 EtOH/AcOH, m.p. 126° (235), 123° (230).

p-Chlorophenyl 2,4,6-trinitrophenyl ether [This prod which should easily be obtd. from C̄ (as KĀ) with 2,4,6-trinitrochlorobenzene (picryl chloride) appears to be unreported.]

p-Chlorophenyl 4-chloro-2-nitrophenyl ether: from C̄ (as KĀ) with 2,5-dichloronitrobenzene on htg. (84.4% yield (230)) (229) (231) (84), pale yel ndls from alc., m.p. 79° (230), 78° (231), 75° (229); b.p. 215–220° at 15 mm (229)

p-Chlorophenyl 4-bromo-2-nitrophenyl ether: from C̄ (as KĀ) with 2,5-dibromonitrobenzene on htg. (91.0% yield (230)) (236), pale yel ndls. from AcOH, m.p. 100–101° (236), 100.5° (230).

Esterification

Esters of inorganic acids. [C̄ with $SOCl_2$ + pyridine in C_6H_6 as directed gives (237) (238) *bis*-(*p*-chlorophenyl) sulfite, b.p. 213–214° at 12 mm., sl. dec.]

[C̄ (3 moles) with PCl_3 (1 mole) at 150° gives (239) *tris*-(*p*-chlorophenyl) phosphite, m.p. 49°, b.p. 296–297° at 15 mm. (corresp. MeI addn. prod., m.p. 71° (239)), note, however, that C̄ with large excess PCl_3 at 100° gives (240) *p*-chlorophenylphosphorous dichloride $Cl.C_6H_4.OPCl_2$, b.p. 128–130° at 12 mm., and di-(*p*-chlorophenyl)phosphorous chloride $(Cl.C_6H_4.O)_2{=}P{-}Cl$, b.p. 225–227° at 11 mm.]

[C̄ (3 moles) with $POCl_3$ (1 mole) under reflux (241), or C̄ with $POCl_3$ in cold alk. soln. (242) (243), or C̄ (as NaĀ) with $POCl_3$ in neutral inert solv. (244), gives tri-(*p*-chlorophenyl) phosphate [Beil. VI-188, VI_1-(102)], m.p. 117° (241), 112° (244) — Note, however, that C̄ with $POCl_3$ in pres. of Mg at 130–140° gives (245) *p*-chlorophenylphosphoryl dichloride, $Cl.C_6H_4.O{-}P(O)Cl_2$ [Beil. VI-188, VI_1-(102)], b.p. 265° at 760 mm. (246) (247), 141° at 12 mm. (246), 95–115° at 0.1 mm. (245), accompanied by di-(*p*-chlorophenyl)-phosphoryl chloride $(Cl.C_6H_4.O)_2P(O)Cl$ [Beil. VI-188], b.p. 164–176° at 0.1 mm. (245); these two products may be hydrolyzed, respectively, to *p*-chlorophenylphosphoric acid [Beil. VI-188] cf. (248), m.p. 80–81° (249), and di-(*p*-chlorophenyl)phosphoric acid [Beil. VI-188], m.p. 126–127° (242), 133–135° cor. (248) (250).]

[For analogous behavior of C̄ with $TiCl_4$ see (251).]

Esters of aliphatic organic acids (see also below under Ⓓ's).

p-Chlorophenyl acetate: from C̄ with Ac_2O + NaOAc (252); m.p. 7–8° (252), b.p. 226–228° (253), 100–102° at 15 mm. (254), 108° at 12.5 mm. (252), 90–92° at 2.5 mm. (61), D_4^{20} = 1.2248 (252). — Note that this prod. with $AlCl_3$ on htg. (255) (254) (61) or C̄ with AcCl + $FeCl_3$ directly (256) gives (100% yield (255)) 4-chloro-2-acetylphenol (5-chloro-2-hydroxyacetophenone) [Beil. VIII-86], m.p. 55° (256), 54° (61), 53.5–54.5° (167), b.p. 97–99° at 2 mm. (61) (corresp. acetate, b.p. 156–157° (140)).

p-Chlorophenyl propionate: from C̄ with propionyl chloride (3:7170) (140) (61); oil, b.p. 234–236° (140), 76–78° at 2 mm. (61). — Note that this prod. with $AlCl_3$ undergoes Fries rearr. giving (140) (61) 4-chloro-2-propionylphenol (5-chloro-2-hydroxypropiophenone), m p. 59.7° (61), 56.5–57.5° (140) (corresp. methyl ether, m.p. 41–42°, b.p. 135–140° at 6 mm. (257)).

p-Chlorophenyl n-butyrate: from C̄ with *n*-butyryl chloride (3:7370) (140) (61); oil, b.p. 249–251° (140), 96–98° at 3 mm. (61). — Note that this prod. with $AlCl_3$ undergoes Fries rearr. giving (140) (61) 4-chloro-2-(*n*-butyryl)phenol (5-chloro-2-hydroxy-*n*-butyrophenone), m.p. 50.5° (61), 49–50° (140); b.p. 108–112° at 3 mm. (61).

p-Chlorophenyl isobutyrate: from C̄ with isobutyric acid (1:1030) + $POCl_3$ (258); m p. 29°, b.p. 120° at 11 mm. (258). — Note that this prod. with $AlCl_3$ undergoes Fries rearr. giving (258) 4-chloro-2-isobutyrylphenol (5-chloro-2-hydroxy-isobutyrophenone), oil, b.p. 130° at 20 mm., D_4^{20} = 1.192, n_{He}^{20} = 1.5521 (258).

[For generally analogous behavior of C̄ with *n*-valeryl chloride (3:7740), *n*-caproyl chloride (3:8168), *n*-heptanoyl chloride (3:8520), *n*-octanoyl chloride (3:8680) see (61); with chloroacetyl chloride (3:5235) see (259); with α-bromo-isovaleryl bromide see (260).]

C̄ (as NaĀ) (2 moles) with $COCl_2$ (3:5000) in C_6H_6 at 130–180° under press. (261) or C̄ (as KĀ) in conc. aq. soln. with $COCl_2$ in toluene (262), or C̄ with trichloromethyl chloroformate (diphsogene) (3:5515) + aq. NaOH (263), gives di-(*p*-chlorophenyl) carbonate [Beil. VI-187], m.p. 147° (263), 144–145° (264).

Esters of aromatic organic acids (see also below under Ⓓ's).

p-Chlorophenyl benzoate: from C̄ with benzoyl chloride (3:6240) (265) (for study of rate at 25° see (268)) in pres. of aq. NaOH (252) (266) (267); m.p. 87–87.5° (138), 87° u.c. (252), 86° (266) (267) — Note that this prod. with $AlCl_3$ undergoes Fries rearr. giving (140) 4-chloro-2-benzoylphenol (5-chloro-2-hydroxybenzophenone), m.p. 95.0–95.5° (138), 94–95° (139), 94° (137), 93–94° (140) (corresp. benzoate, m.p. 112° (139)).

p-Chlorophenyl cinnamate: from C̄ with cinnamoyl chloride (3:0330) (68% yield (260)), m.p. 105° (260) (269).

—— **_p_-Chlorophenyl methyl ether (_p_-chloroanisole):** oil. (See 3:6300.)

—— **_p_-Chlorophenyl ethyl ether (_p_-chlorophenetole):** m.p. 20–21°. (See 3:0090.)

—— **_p_-Chlorophenyl acetate:** m p. 7–8° (252). [For further details see above under esters of C̄ with aliphatic organic acids.]

Ⓓ **_p_-Chlorophenyl benzoate:** m.p. 87.0–87.5° (138), 87° u.c. (252), 86° (266) (267) [From C̄ with benzoyl chloride in pres. of aq. NaOH (252) (266) (267) (see also above under esters of C̄ with aromatic organic acids).]

—— **_p_-Chlorophenyl _o_-nitrobenzoate:** unreported.

Ⓓ **_p_-Chlorophenyl _m_-nitrobenzoate:** m.p. 124.5° (252). [From C̄ with *m*-nitrobenzoyl chloride + aq. NaOH (252).]

Ⓓ **_p_-Chlorophenyl _p_-nitrobenzoate:** m.p. 171° (270).

Ⓓ **_p_-Chlorophenyl 3,5-dinitrobenzoate:** m.p. 186° (271).

—— **_p_-Chlorophenyl benzenesulfonate:** unreported.

—— *p*-Chlorophenyl *p*-toluenesulfonate: unreported.

Ⓓ *p*-Chlorophenyl benzyl ether: ndls. from alc., m.p. 71° (272), 70–71° (273). [Note, however, that C̄ with benzyl chloride (3:8535) + $AlCl_3$ gives not only this prod. but also (273) cf. (274) some Fries rearr. prod., viz., 4-chloro-2-benzylphenol (5-chloro-2-hydroxydiphenylmethane), m p 48–49° (273), 48.5° (274) (corresp. benzoate, m.p. 54–55°, benzenesulfonate, m.p. 68–69°, *p*-toluenesulfonate, m.p. 75 0–75 5° (273)).]

Ⓓ *p*-Chlorophenyl *p*-nitrobenzyl ether: cryst. from alc., m.p. 101.3° (275). [From C̄ + *p*-nitrobenzyl chloride (m p. 71°) (or *p*-nitrobenzyl bromide, m.p. 99°) in alc. NaOEt (275).]

Ⓓ *p*-Chlorophenyl 2,4-dinitrophenyl ether: yel. tbls. from 1:2 EtOH/AcOH, m p. 126° (235), 123° (230). [From C̄ (as KĀ (230) or NaĀ (235)) with 2,4-dinitrochlorobenzene (m.p. 51°) on htg (97% yield (230))]

Ⓓ *p*-Chlorophenoxyacetic acid (3:4375): pr. from hot aq., m.p. 156.7–157 2° cor. (279), 155–156 5° u.c. (276), 155–156° (277), 154–155° (278). [From C̄ with chloroacetic acid in aq alk (279) (276) (277) (278)]

—— *p*-Chlorophenyl *N*-phenylcarbamate: cryst. from alc., m p. 138° (280), 137–138° (263). [From C̄ (as NaĀ) with phenylisocyanide dichloride on htg. (280); note, however, prepn. from C̄ + phenyl isocyanate has *not* been reported.

Ⓓ *p*-Chlorophenyl *N*-(*p*-bromophenyl)carbamate: white pl. from C_6H_6/EtOAc, m.p 196–197° cor. (281). [From C̄ with *p*-bromobenzazide (281) in lgr. (281).]

Ⓓ *p*-Chlorophenyl *N*-(*p*-iodophenyl)carbamate: m p. 214–215° (282). [From C̄ with *p*-iodobenzazide (282) in lgr (282)]

Ⓓ *p*-Chlorophenyl *N*-(*m*-nitrophenyl)carbamate: white pl. from lgr , m p. 136° u.c., 139° cor. (283). [From C̄ with *m*-nitrobenzazide (283) or *m*-nitrophenyl isocyanate (283) in lgr. (283)]

Ⓓ *p*-Chlorophenyl *N*-(*p*-nitrophenyl)carbamate: pale yel. rods from lgr., m.p. 196° cor. (284). [From C̄ with *p*-nitrobenzazide (284) in lgr. (284).]

Ⓓ *p*-Chlorophenyl *N*-(3,5-dinitrophenyl)carbamate: yel pl. from C_6H_6/EtOAc, m.p. 197–198° (285). [From C̄ with 3,5-dinitrobenzazide (285) in lgr. (285).]

Ⓓ *p*-Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: pale yel. pl. from lgr., m.p. 206–207° u.c., 212–213° cor (286) [From C̄ with 3,5-dinitro-4-methylbenzazide (286) in lgr. (286)]

Ⓓ *p*-Chlorophenyl *N*-(α-naphthyl)carbamate: m p. 165–166° (287). [From C̄ with α-naphthyl isocyanate in lgr (287).]

Ⓓ *p*-Chlorophenyl *N*-(β-naphthyl)carbamate: pl. from lgr , m p 165–166° u.c., 169–170° cor (288) [From C̄ with β-naphthyl isocyanate (288) in lgr. (288).]

Ⓓ *p*-Chlorophenyl *N*,*N*-diphenylcarbamate: m.p. 97° (289) [From C̄ with *N*,*N*-diphenylcarbamyl chloride (289)]

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(81) Vorozhtzov, Karlash, Russ. 30,689, June 30, 1933; *Cent.* **1934**, I 767; *C.A.* **28**, 5834 (1934). (82) Böeseken, Metz, *Rec. trav. chim.* **54**, 346, 350 (1935). (83) Fichter, Adler, *Helv. Chim. Acta* **9**, 279–281 (1926). (84) Groves, Turner, Sharp, *J. Chem. Soc.* **1929**, 516, 519. (85) Roberts, Soper, *J. Chem. Soc.* **1932**, 1982. (86) Soper, Smith, *J. Chem. Soc.* **1926**, 1589. (87) Thomas, *J. Am. Chem. Soc.* **63**, 629–630 (1941). (88) Raiford, Miller, *J. Am. Chem. Soc.* **55**, 2127 (1933). (89) Hunter, Joyce, *J. Am. Chem. Soc.* **39**, 2643–2644 (1917). (90) Fox, Turner, *J. Chem. Soc.* **1930**, 1861.

(91) [illegible] J. Am. Chem. Soc. 48, 419 (1926). (92) Kohn, Rosenfeld, *Monatsh.* **46**, 100–107, [illegible] (94) Kohn, Kramer, [illegible]), 545–547 (1928). (96) [illegible] 25, 1632 (1931)]. (97) [illegible] 1, 17–19, *C.A.* **33**, 8143 [illegible] *Soc.* **16**, 477–478 (1939). [illegible] Girod, *Compt. rend.* **186**, 1553–1555 (1928).

(101) [illegible] *Ann.* [illegible] 7, 101–105 (1870). (102) Mottier, *Arch. sci. phys. nat.* **16**, [illegible] (103) Neunhoeffer, *Ber.* **68**, 1777–1778 [illegible] –630 (1930). (105) Plazek, *Roczniki* [illegible] –1505 (1931)]. (106) Reverdin, *Ber.* [illegible] *Soc. Japan* **1925**, No. 517, 247–252; [illegible] *für Chemie*, **1867**, 206; *Jahresber.* **1867**, 613. (109) Schouten, *Rec. trav. chim.* **56**, 555 (1937). (110) Petersen, Baehr-Predari, *Ann.* **157**, 161 (1871).

(111) Tarbell, Mallatt, Wilson, *J. Am. Chem. Soc.* **64**, 2229 (1942). (112) Rasbevskaya, Zil'berman, Chernyarskaya, Shirvskaya, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 499–505 (1937); *Cent.* **1938**, I 58, *C.A.* **31**, 6212 (1937). (113) Petersen, Baehr-Predari, *Ann.* **157**, 128–147 (1871). (114) Gauntlett, Smiles, *J. Chem. Soc.* **127**, 2745–2746 (1925). (115) Hamer, Pinching, Acree, *J. Research Natl. Bur. Standards* **31**, 291–304 (1943). (116) Schoepfle, Van Natta, Clarkson; *J. Am. Chem. Soc.* **50**, 1172–1174 (1928). (117) Bayer and Co., Ger. 234,851, May 20, 1911, *Cent.* **1911**, I 1769, *C.A.* **5**, 2912 (1911). (118) Hart, Andersen, *J. Am. Chem. Soc.* **57**, 1060 (1935). (119) Kalinowski, *Roczniki Chem.* **9**, 131–147 (1929); *Cent.* **1929**, I 2301; *C.A.* **23**, 3216 (1929). (120) Engelmann (to du Pont Co.), U.S. 1,748,331, Feb. 25, 1930; *Cent.* **1930**, II 802; *C.A.* **24**, 1927 (1930).

(121) Engelmann, Funk (to du Pont Co.), U.S. 1,801,145, April 14, 1931; *Cent.* **1932**, I 571; *C.A.* **25**, 3430 (1931). (122) Hinsberg, Ger. 538,376, Nov. 14, 1931; *Cent.* **1932**, I 2094; [*C.A.* **26**, 1617 (1932)]. (123) F. Bayer and Co., Ger. 132,475, June 9, 1902; *Cent.* **1902**, II 82. (124) Buehler, Bass, Darling, Lubs, *J. Am. Chem. Soc.* **62**, 890–891 (1940). (125) Weiler, Berres (to I.G.), Ger. 510,447, Oct. 18, 1930, *Cent.* **1931**, I 2115, *C.A.* **25**, 974 (1931). (126) Hanus, *J. prakt. Chem.* (2) **158**, 253 (1941). (127) Zinke, Hanus, Ziegler, *J. prakt. Chem.* (2) **152**, 142 (1939). (128) Sen, Ray, *J. Indian Chem. Soc* **9**, 176 (1932). (129) Duff, *J. Chem. Soc.* **1941**, 547–550. (130) Pauly, Schanz, *Ber.* **56**, 979–985 (1923).

(131) Haakh, Smola, Austrian 141,159, March 25, 1935; *Cent.* **1935**, II 439; *C.A.* **29**, 4021 (1935). (132) Zeitner, Landau, Ger. 258,887, April 17, 1913; *Cent.* **1913**, I 1641; [*C.A.* **7**, 2996 (1913)]. (133) Hasse, *Ber.* **10**, 2190 (1877). (134) Varnholt, *J. prakt. Chem.* (2) **36**, 17–22 (1887). (135) Chem. Fabrik von Heyden, Ger. 33,635; *Friedländer* **1**, 234 (1877–1887). (136) Dhar, *J. Chem. Soc.* **117**, 1008 (1920). (137) Pieroni, *Gazz. chim. ital.* **62**, 390 (1932). (138) Hayashi, *J. prakt. Chem* (2) **123**, 298–299, 304 (1929). (139) Arventi, *Bull. soc. chim.* (5) **3**, 603 (1936). (140) [illegible] *Ann.* **41**[illegible], 101–108, 186–188 (1926).

(141 [illegible] Ullma [illegible] and C [illegible] Hayas [illegible] (1931) [illegible] 46, 18 [illegible]

[illegible] (1932). (160) Schwenk (to General Aniline Works), U.S. 1,890,866, Dec. 13, 1932; *Cent.* **1933**, II 613; [*C.A.* **27**, 1642 (1933)].

(161) [illegible] (to I.G.), Ger. [illegible] **1932**, I 591; [*C.A.* **26**, 1142 (1932)]. (162) [illegible] **14**, [illegible] (163) Hayashi, *J. Chem. Soc.* **1930**, 1513–1518. (164) [illegible] **131**, [illegible] (165) Waldmann, Mathio-

wetz, *Ber.* **64**, 1718 (1931). (167) Wittig, *Ber.* **57**, 88–91 (1924). (168) Mayer 1974 (1928). (169) Chakravarti, Dutta, *J. Ind* *J. Chem. Soc.* **107**, 1642, 1644 (1915).

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(181) F. Dunning, B. Dunning, W. Drake, *J. Am. Chem. Soc.* **53**, 3466–3469 (1931). (182) Richter, *Ber.* **49**, 1024–1025 (1916). (183) Muth (to I.G.), Ger. 568,944, Jan. 1, 1933; *Cent.* **1933**, I 2280; *C.A.* **27**, 2696 (1933).

(185) Hilditch, Smiles, *J. Chem Soc.*

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(1871). (188) Faust, *Ber.* **6**, 1022–1023 (1873). (189) Boehringer und Söhne, Ger. 269,544, Jan. 22, 1914, *Cent.* **1914**, I 591–592; [*C.A.* **8**, 2221 (1914)]. (190) Bayer and Co., Ger. 249,939, Aug. 1, 1912, *Cent.* **1912**

(191) Burroughs (2,041,592, May 19, 1936; *Cent.* **1937**, I 1016; *C.A.*,

1908, I 1051; *C A.* **2**, 1700 (1908). (193) Tijr

1908, I 1051; *C.A.* **2**, 1700–1701 (1908). (194)

370 (1912); *C.A.* **36**, 5469 (1942)

Oct. 27, 1932; *Cent.* **1933**, I 675;

1908, *Cent.* **1909**, I 600; [*C.A.* **3**,

Murray, Gordon, *J. Am. Chem.*

Chim. Acta **11**, 27 (1928). (200) Jenkins, *J. Chem. Soc.* **1939**, 1139.

(201) Baddeley, Bennett, Glasstone, Jones, *J. Chem. Soc.* **1935**, 1827–1830. (202) Mizutani, *Z. physik. Chem.* **118**, 326 (1925). (203) Mizutani, *Z. physik. Chem.* **118**, 331 (1925). (204) Schwarzenbach, Egli, *Helv. Chim. Acta* **17**, 1176–1182 (1934). (205) Naegeli, *Kolloid-Chem. Beihefte* **21**, 344,387 (1926). (206) Hantzsch, Mai, *Ber.* **28**, 978 (1895). (207) Schulke-Mayr, Flemming, Ger. 247,410, May 5, 1929; *Cent.* **1912**, II 165; [*C.A.* **6**, 2674 (1912)]. (208) Perrier,

2815. (213) Bradfield, Jones, *J. Chem. Soc.* **1929**, 3081.

(2 Bayer and Co., Ger. 282,991, March

10; *Cent.* **1910**, I 974; [*C.A.* **4**, 2029–2030 (1910)]. (222) Ehlotzky, *Monatsh.* **30**, 664–665 (1909). (223) Nieuwland, Vogt, Foohey, *J. Am. Chem. Soc.* **52**, 1023 (1930). (224) Ruhemann, *Ber.* **54**, 918,921 (1921). (225) Suter, Green, *J. Am. Chem. Soc.* **59**, 2579 (1937). (226) Brewster, Stevenson, *J. Am. Chem. Soc.* **62**, 3144–3146 (1940). (227) Langham, Brewster, Gilman, *J. Am. Chem. Soc.* **63**, 545–549 (1941). (228) Mailhe, Murat, *Compt. rend.* **154**, 601–603 (1912); *Bull. soc. chim.* (4) **11**, 329–331 (1912). (229) LeFevre, Saunders, Turner, *J. Chem. Soc.* **1927**, 1170–1173. (230) Raiford, Colbert, *J. Am. Chem. Soc.* **48**, 2659–2660 (1926).

(231) McCombie, Macmillan, Scarborough, *J. Chem. Soc.* **1931**, 533–534. (232) Roberts, Turner, *J. Chem. So* **1929**, 2364–2365. (234) Hester (1942). (235) Bost, Nicholso *Chem. Soc.* **1930**, 1119–1120. (237) Richter, *Ber.* **49**, 2344 (1916). (238) B.A.S.F., Ger. 303,033, Jan. 14, 1918; *Cent.* **1918**, I 499–500; *C.A.* **13**, 324 (1919). (239) Michaelis, Kaehne, Rocholl, *Ber.* **31**, 1053 (1898). (240) Strecker, Grossmann, *Ber.* **49**, 85 (1916). 44). , **25**,

Nachmann, *Helv. Chim. Acta* **9**, 425–427 (1926). (249) Kekulé, Barbaglia, *Ber.* **5**, 877 (1872). (250) Kosolapoff, *J. Am. Chem. Soc.* **64**, 2982–2983 (1942).

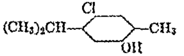
(251) Luchinsku, *J Gen. Chem.* (*U S S.R*) **7**, 2044–2047 (1937), *Cent.* **1938**, I 3909; *C.A.* **32**, 519 (1938). (252) Wohlleben, *Ber.* **42**, 4372–4373 (1909). (253) Seelig, *J. prakt. Chem.* (2) **39**, 175 (1889). (254) Karrer, Yen, Reichstein, *Helv. Chim. Acta* **13**, 1315 (1930). (255) von Auwers, Wittig, *Ber.* **57**, 1275 (1924). (256) Nencki, Stoeber, *Ber.* **30**, 1769 (1897). (257) Chakravarti, Majumdar, *J. Indian Chem. Soc.* **15**, 137 (1938). (258) von Auwers, Baum, Lorenz, *J. prakt. Chem.* (2) **115**, 91–92 (1927) (259) Fries, Hasselbach, Schroder, *Ann.* **405**, 368–370 (1914). (260) Skraup, Beng, *Ber.* **60**, 946, 948 (1927)

(261) von Heyden, Ger. 81,375, *Friedländer* **4**, 1117 (1894–1897). (262) Barral, Morel, *Bull. soc. chim.* (3) **21**, 722–727 (1899). (263) Melnikow, *J. prakt. Chem.* (2) **127**, 236–237 (1930). (264) Barral, *Compt. rend.* **126**, 908 (1898); **138**, 910 (1904). (265) Mosso, *Jahresber.* **1887**, 1301. (266) Autenrieth, Muhlinghaus, *Ber.* **39**, 4102 (1906) (267) Autenrieth, *Arch. Pharm.* **233**, 41 (1895). (268) Bernoulli, St. Goar, *Helv. Chim. Acta* **9**, 754–755 (1926). (269) Anschütz, *Ber.* **60**, 1322 (1927). (270) I.G., Danish 59,316, Dec. 22, 1941; *Cent* **1942**, II 812; not in *C.A.*

(271) Tseng, Ph.D. Thesis, M.I.T. (unpublished). (272) Baw, *J. Indian Chem. Soc.* **3**, 104 (1926). (273) Huston, Guile, Chen, Headley, Warren, Baur, Mate, *J. Am. Chem. Soc.* **55**, 4641–4642 (1933). (274) Klarmann, Gates, Shternov, *J. Am. Chem. Soc.* **54**, 3323 (1932). (275) Lyman, Reid, *J Am. Chem. Soc.* **42**, 616 (1920). (276) Koelsch, *J. Am. Chem. Soc.* **53**, 304–305 (1931). (277) Minton, Stephen, *J Chem. Soc.* **121**, 1600 (1922). (278) Behaghel, *J. prakt. Chem.* (2) **114**, 297–298 (1926) (279) Hayes, Branch, *J. Am. Chem. Soc.* **65**, 1555 (1943) (280) Hantzsch, Mai, *Ber* **28**, 979–980 (1895).

(281) Sah, Cheng, *Rec. trav chim.* **58**, 592–593 (1939) (282) Sah, Young, *Rec. trav. chim.* **59**, 357–363 (1940), *C.A.* **35**, 4363 (1941) (283) Sah, Woo, *Rec. trav. chim.* **58**, 1014–1015 (1939). (284) Sah, Cheng, *Rec trav chim.* **58**, 596–597 (1939) (285) Sah, Ma, *J Chinese Chem. Soc.* **2**, 230–231 (1934). (286) Sah, *Rec. trav. chim* **58**, 587–588 (1939). (287) French, Wirtel, *J. Am. Chem. Soc.* **48**, 1736–1739 (1926). (288) Sah, *Rec. trav chim* **58**, 454–458 (1939). (289) Korczynski, *Gazz. chim. ital.* **53**, 96 (1923).

3:0480 4-CHLORO-5-ISOPROPYL-2-METHYLPHENOL $C_{10}H_{13}OCl$ Beil. VI —
(*p*-(5)Chlorocarvacrol) VI_1—
VI_2-(494)



M.P. 42–43° (1) **B.P. 158°** at 52 mm. (2)
138–140° at 12 mm. (3)
135–136° at 12 mm. (1)

Volatile with steam.

[For prepn of C̄ from 2-hydroxy-*p*-cymene (carvacrol)(1.1760) with Cl_2 (4) or with SO_2Cl_2 (1) see indic. refs; from 4-chloro-5-isopropyl-2-methyl-aniline (5-chloro-2-amino-*p*-cymene) (2) via diazotization and subsequent hydrolysis see (2), from 5-amino-2-hydroxy-*p*-cymene (5-aminocarvacrol) via diazotization and subsequent reactn. with aq. HCl + Cu powder see (3); from 4-chloro-2-methylphenol (*p*-chloro-*o*-cresol) (3 0780) by reactn. with isopropyl alc. + H_2SO_4 at 80° or in decalin soln. with propylene + $AlCl_3$ see (5).]

[C̄ has outstanding bactericidal properties and is used ("Carvasept" (6)) as disinfectant, antiseptic, germicide, preservative (7), and anthelmintic (8) (9), for reviews of bactericidal actn. see (10) (11) (12) (13).]

[For solubilization of C̄ with soap solns. (14) and use of C̄ in soap solns. as disinfectant see (14) (15) (16); for prepn of esters of C̄, e g, the carbonate, m.p. 83–84° (from C̄ + dil. aq NaOH + phosgene), or the salicylate, m.p. 60–61° (from C̄ + salicylic acid + $POCl_3$), see (17); for mercuration of C̄ see (18), for use of C̄ in mouth wash see (19).]

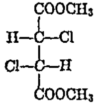
Ⓓ **4-Chloro-5-isopropyl-2-methylphenyl ethyl ether:** m.p. 54–56° (17). [From C̄ in dil aq. NaOH with Et_2SO_4 (17)]

Ⓓ **4-Chloro-5-isopropyl-2-methylphenoxyacetic acid:** m p. 160–161° (17). [From C̄ in dil. aq NaOH with chloroacetic acid (17)]

3:0480 (1) Chem. Fabrik von Heyden, A.G., French 736,304, Nov. 22, 1932; *Cent.* **1933**, 1653.
(3) Philipp (to Chem. Fabrik von Heyden,
(4) Momm, Brit. 411,430, July 5, 1934;
,717, April 10, 1930; *Cent.* **1930**, II 984.
to Chem. Fabrik von Heyden, A.G.), Ger.
ıson, Stoughton, Bass, *J. Pharmacol.* **56**,
)36). (9) Kochmann, *Arch. exptl. Path.*
Pharmakol. **161**, 190–205 (1931); ... 2060; *C.A.* **26**, 1330 (1932). (10) Heading, *Pharm. J.* **138**, 321–322 (1937); *Chemist and Druggist* **126**, 392–393 (1937); *Cent.* **1937**, II 2208. (11) Weichardt, *Münch. Med. Wochschr.* **78**, 1515–1516 (1931). (12) Kuhn, *Med. Klin.* **28**, 790–791 (1932); *Cent.* **1932**, II 1036; *Med. Klin.* **26**, 1047–1048 (1930); *Cent.* **1930**, II 2282.

Gelinsky, Ger. 649,126, Aug. 1
Heyden), U.S. 1,957,908, May
4180 (1934). (18) Christians
C.A. **35**, 7657 (1941). (19) P
French 693,083, Nov. 14, 1930; *Cent.* **1931**, I 1481.

3:0485 DIMETHYL *d,l*-α,α'-DICHLOROSUCCINATE $C_6H_8O_4Cl_2$ Beil. II —
(Dimethyl *allo*-dichlorosuccinate; dimethyl isodichlorosuccinate) II_1-(267) II_2-(557)

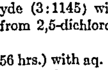


M.P. 43° (1) **B.P. 116.5–120.5° cor. at 12.5 mm.** (2)
42–43° (2) **105° at 3 mm.** (1)

[For prepn. of $\bar{C}$ from *d,l*-α,α'-dichlorosuccinic acid (3:4711) in MeOH with H_2SO_4 at ord. temp. see (3); from dimethyl *d,l*-tartrate (1:2385) (1) or from dimethyl low-melting β-chloro-*d,l*-malate [Beil. III-438, III_2-(290)] (2) with $SOCl_2$ in pyridine see indic. refs.]
$\bar{C}$ with dimethylaniline loses 1 HCl yielding (1) dimethyl chlorofumarate (3:6582).

3:0485 (1) Darzens, Séjourne, *Compt. rend.* **154**, 1616 (1912). (2) Kuhn, Wagner-Jauregg, *Ber.* **61**, 514 (1928). (3) Holmberg, *Arkiv. Kemi, Mineral. Geol.* **8**, No. 2, 17, 33 (1920); *Cent.* **1921**, I 820; *C.A.* **16**, 2116 (1922).

3:0490 2,5-DICHLOROBENZAL (DI)CHLORIDE $C_7H_4Cl_4$ **Beil. V - 302**
V_1—
V_2-(234)



M.P. 43° (1) B.P. 118–120° at 14 mm. (1)
42° (2) (3)

Cryst. from $CHCl_3$; very eas. sol. org. solvents but spar. sol. in aq. — $\bar{C}$ has faint but not disagreeable odor. — Volatile with steam.
[For prepn. of $\bar{C}$ from 2,5-dichlorobenzaldehyde (3:1145) with PCl_5 (78% yield (1)) or with $ClSO_3H$ in $CHCl_3$ (3) see indic. refs.; from 2,5-dichlorotoluene (3:6245) at b.p. with Cl_2 see (2).]
$\bar{C}$ on hydrolysis, e g., by protracted refluxing (56 hrs.) with aq. + $CaCO_3$ (2), or by treatment with fumg. H_2SO_4 (3), yields 2,5-dichlorobenzaldehyde (3:1145). [For study of rate of hydrolysis in 50% alc. at 83.5° see (1).]

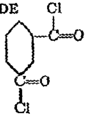
3:0490 (1) Asinger, Lock, *Monatsh.* **62**, 336–337 (1933). (2) de Crauw, *Rec. trav. chim.* **50**, 773 (1931). (3) Gnehm, Schüle, *Ann.* **299**, 350–360 (1898).

CHAPTER III

DIVISION A. SOLIDS

(3:0500–3:0999)

3:0520 ISOPHTHALYL (DI)CHLORIDE $C_8H_4O_2Cl_2$ Beil. IX - 834
(Isophthaloyl dichloride) IX_1-(372)



M.P.		B.P.			
43–44°	(1)	276°		(3)	$D_4^{46.9} = 1.3872$ (9)
42–43°	(2)	200° (?)	at 15 mm.	(7)	$n_D^{46.9} = 1.56999$ (9)
41–43°	(18)	156°	at 15 mm.	(8)	
41°	(3) (4)	142.6–143°	at 14 mm.	(5)	
40.5–41°	(5)	143–144°	at 13 mm.	(2)	
40°	(6)	136°	at 11 mm.	(18)	

Prisms from pet. ether.

[For prepn. of $\bar{C}$ from isophthalic acid (1:0900) with PCl_5 (3) in a s.t. at 200° (10) or in $POCl_3$ (8) see indic. refs.; with AcCl (3:7065) in s.t. at 130° for 8 hrs. see (1); with $SOCl_2$ (yield: 100% (6), 92% (18), 67% (2), 62% (7)) (5) see indic. refs.; for prepn. of $\bar{C}$ from 1,3-*bis*-(trichloromethyl)benzene by partial catalytic hydrolysis see (4) (17).]

$\bar{C}$ with excess MeOH yields (11) dimethyl isophthalate (1:2214), m.p. 67–68°; cf. also under isophthalic acid (1:0900); $\bar{C}$ with excess phenol yields (3) diphenyl isophthalate, m.p. 120° (3).

[*$\bar{C}$ on cat. hydrogenation in xylene with Pd cat. as specified (12) gives 83% yield isophthalaldehyde* [Beil. VII-675, VII_1-(364)], cryst. from alc., m.p. 88–89° (12) (dioxime, m.p. 178°; *bis*-phenylhydrazone, m.p. 242–244° (12)).]

[$\bar{C}$ with $AlCl_3$ + benzene yields (13) 1,3-dibenzoylbenzene (isophthalophenone) [Beil. VII-829, VII_1-(443)], m.p. 100–101° (dioxime, m.p. 70–75° (10)); for corresp. reactn. of $\bar{C}$ with *m*-xylene (1:7420) see (14); for corresp. reactn. of $\bar{C}$ with anisole (1:7445) see (15).]

[For reactns. of $\bar{C}$ with ethyl sodio-acetoacetate see (8) and with ethyl sodio-cyanoacetate see (16).] [For behavior of $\bar{C}$ with diazomethane see (18).]

$\bar{C}$ on hydrolysis yields isophthalic acid (1:0900) q.v. for further characterization.

3:0520 (1) Liebermann, Kardos, *Ber.* **46**, 211 (1913). (2) Reindel, Siegel, *Ber.* **56**, 1554 (1923). (3) Schreder, *Ber.* **7**, 708 (1874). (4) I.G., French 820,097, Nov. 16, 1937; *Cent.* **1938**, I 1661; *C.A.* **32**, 3422 (1938). (5) Kohlrausch, Pongratz, Stockmair, *Monatsh.* **67**, 109 (1935). (6) Meyer, *Monatsh.* **22**, 436 (1901). (7) McMaster, Ahmann, *J. Am. Chem. Soc.* **50**, 148 (1928). (8) Ruggli, Gassenmeier, *Helv. Chim. Acta* **22**, 499–500 (1939). (9) von Auwers, Schmidt, *Ber.* **46**, 481 (1913). (10) Münchmeyer, *Ber.* **19**, 1848–1849 (1886).

(11) Baeyer, Villiger, *Ann.* **276**, 258 (1893). (12) Rosenmund, Zetsche, *Ber.* **54**, 2890 (1921). (13) Ador, *Ber.* **13**, 320 (1880). (14) Clar, John, Hawran, *Ber.* **62**, 945 (1929). (15) Weiss, Chledowski, *Monatsh.* **65**, 358, 362–363 (1935). (16) Sacher, *Bull. soc. chim.* (3) **11**, 1097 (1894). (17) I.G., Ger. 708,149, June 5, 1941; *C.A.* **37**, 2746 (1943). (18) Ruggli, Knecht, *Helv. chim. Acta* **27**, 1108–1115 (1944); *C.A.* **39**, 4857 (1945).

3:0525 16-CHLOROHEXADECANOL-1 $C_{16}H_{33}OCl$ Beil. S.N. 24
(ω-Chloro-*n*-hexadecyl alcohol; ω-Chloropalmityl alcohol)

$CH_2—(CH_2)_{14}.CH_2OH$
|
Cl

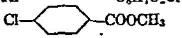
M.P. 43° (1)

Colorless cryst. from lt. pet.

[For prepn. of C̄ from α,ω-hexadecamethylene glycol [Beil. I_2-(565)] (m.p. 87–88° (1)) with $SOCl_2$ + dimethylaniline in C_6H_6 (60% yield) see (1); note that a little 1,16-dichlorohexadecane, cryst. from MeOH, m.p. 47°, is also formed.]

3:0525 (1) Bennett, Gudgeon, *J. Chem. Soc.* **1938**, 1679–1681.

3:0535 METHYL *p*-CHLOROBENZOATE $C_8H_7O_2Cl$ Beil. IX - 340
IX_1—



M.P. 44° (1)
43–43.5° (2) (6)
43° (3) (4)
42° (5)
34° (9)

[For prepn. of C̄ from *p*-chlorobenzoic acid (3:4940) with MeOH + HCl (2) or MeOH + H_2SO_4 (2) (6) see indic. refs.; from AgĀ + MeI in s.t. at 100° see (5); from *p*-chlorobenzoyl chloride (3:6550) with MeOH see (3).]

C̄ on htg. with sirupy H_3PO_4 at 200° yields (7) *p*-chlorobenzoic acid (3:4940), dimethyl ether, and probably some *p*-chlorotoluene (3:8287).

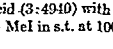
C̄ added to 5–6 pts. very conc. HNO_3 at 0°, poured onto ice, yields (3) methyl 4-chloro-3-nitrobenzoate [Beil. IX-402], cryst. from MeOH, m.p. 83° (3).

[C̄ with Na + methyl acetate condenses giving (60% yield (6)) methyl *p*-chlorobenzoylacetate, b.p. 172° at 12 mm., m.p. 36–37° (6); this prod. with excess phenylhydrazine in alc. + AcOH gives on htg. 3-(*p*-chlorophenyl)-1-phenylpyrazolone-5, cr. cryst. from AcOH, m.p. 140° (6); corresp. prod. from *p*-nitrophenylhydrazine, m.p. 200–205° (6).]

C̄ on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + *p*-chlorobenzoic acid (3:4940). [For studies of hydrolysis under various cond. see (2) (4).] — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *p*-chlorobenzoic acid (3:4940).

3:0535 (1) Jaeger, *Z. Krist.* **42**, 22 (1907). (2) Kellas, *Z. physik. Chem.* **24**, 243–252 (1897). (3) Montagne, *Rec. trav. chim.* **19**, 55–56, 61–64 (1900). (4) Jones, McCombie, Scarborough, *J. Chem. Soc.* **123**, 2694–2697 (1923). (5) Emmerling, *Ber.* **8**, 883 (1875). (6) Wahl, Rolland, *Ann. chim.* (10) **10**, 9–12, 15–17 (1928). (7) Raikow, Tischkow, *Chem. Ztg.* **29**, 1269 (1905). (8) Berger, *Rec. trav. chim.* **43**, 170 (1924). (9) Kahovec, Wagner, *Monatsh.* **74**, 285 (1943).

3:0550 3,4-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII - 238
VII_1-(134)



M.P. 44° (1) **B.P. 247–248° (2)**
43–44° (2)
42.0–42.6° (3)

Colorless ndls. from alc. (1), odor like benzaldehyde (2). — Eas. volatile with steam (2) (3).

[For prepn. of C̄ from 3,4-dichlorotoluene (3:6355) via chlorination to 3,4-dichlorobenzal

(di)chloride (3:6876) and hydrolysis of the latter with fumg. H_2SO_4 (5% SO_3) (36% yield (3)), conc. H_2SO_4 (4), or $CaCO_3 + H_2O$ (40% yield (3)) see (2) (3) (4); for prepn. from 4-chloro-3-nitrobenzaldehyde via reduction, diazotization, etc., see (1).]

C̄ with satd. aq. $NaHSO_3$ yields a cpd C̄.$NaHSO_3$ (3). [Use in purification of C̄ (3).]

C̄ on oxidn. with $KMnO_4$ yields (2) 3,4-dichlorobenzoic acid (3:4925), m.p. 201–202° (3). — C̄ with conc. aq. KOH undergoes Cannizzaro reactn. yielding 3,4-dichlorobenzyl alcohol, ndls. from aq., m.p. 38° (3), and 3,4-dichlorobenzoic acid (see above).

C̄ on nitration as specified (5) (4) gives (71% yield (4)) 3,4-dichloro-6-nitrobenzaldehyde [Beil. VII₁-(144)], yel. pr. from C_6H_6, m.p. 73° (5). [This product with $NH_4OH/AgNO_3$ *is oxidized (4) to 3,4-dichloro-6-nitrobenzoic acid, cryst. from* C_6H_6, *m.p. 165° (6).*]

[For conversion of C̄ to 3,4-dichlorostyrene (7) (8) cf. (9) via reaction with MeMgI giving (73% yield (7)) 3,4-dichlorophenyl-methyl-carbinol (7) (8) and dehydration of latter with $KHSO_4$ (yields 83% (8), 64% (7)) see indic. refs.]

(D) **3,4-Dichlorobenzaldoxime** (*anti* form): m.p. 114–115° (2), 118–119° (1). [The *syn* isomer, ndls. from alc., m.p. 120° rap. htg., is converted by fusion (2) to the *anti* form.]

—— **3,4-Dichlorobenzaldehyde phenylhydrazone:** unrecorded.

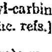
(D) **3,4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** or. ndls., m.p. 276–277° (1).

—— **3,4-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.

—— **3,4-Dichlorobenzaldehyde semicarbazone:** unrecorded.

3:0550 (1) Hodgson, Beard, *J. Chem. Soc.* **1927**, 25. (2) Erdmann, Schwechten, *Ann.* **260**, 72–73 (1890). (3) Kraay, *Rec. trav. chim.* **49**, 1086 (1930). (4) Ruggli, Zaeslin, Lang, *Helv. Chim. Acta* **21**, 1248 (1938). (5) Hoechst Farbwerke, Ger. 254,467, Dec. 3, 1912; *Cent.* **1913**, I 199. (6) Ruggli, Zaeslin, *Helv. Chim. Acta* **19**, 437 (1936). (7) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 863–864 (1946). (8) Brooks, *J. Am. Chem. Soc.* **66**, 1295–1297 (1944). (9) Michalek, Clark, *Chem. & Eng. News* **22**, 1559–1563 (1944).

3:0560 2,4-DICHLOROPHENOL $C_6H_4OCl_2$ **Beil. VI - 189**
VI₁-(103)
VI₂-(178)



M.P.		B.P.		
45°	(1) (2)	210.2–211.5° u.c.	(18)	D^{25}_{-} = 1.4723 (8)
43–44°	(17)	209–211°	(6) (11)	n^{25}_{D} = 1.1729 (8)
43°	(3) (4)	209–210°	(4)	
	(16) (18)	206–208° u.c. at 753 mm.	(7)	
42°	(5)	106.2–107.6° at 14–16 mm.	(3)	
41–42°	(11)			

Colorless ndls. from C_6H_6. — C̄ has unpleasant and persistent odor suggesting iodoform (1) (for study of strength of odor of aq. solns. of C̄ see (1)). — C̄ is spar. sol. aq. (100 g. aq. at 20° dis. 0.45 g. C̄), but is eas. sol. alc., ether, C_6H_6, or $CHCl_3$. — C̄ is volatile with steam; *note, however, that from alk. soln. C̄ is not volatile with steam* (dif. and sepn. from 2-chlorophenol (3:5980) or 4-chlorophenol (3:0475) (9)), although C̄ is volatile with steam from aq. solns. contg. $PbCO_3$ (dif. and sepn. of C̄ from 2,4,6-trichlorophenol (3:1673) (9)). — Note that comml. C̄ often contains 2,4,6-trichlorophenol, and that C̄ prepd. by chlorination of phenol may cont. 2,6-dichlorophenol (3:1595).

[For prepn. of C̄ from *p*-chlorophenol (3:0475) or *o*-chlorophenol (3:5980) with Cl_2 (1 mole) in AcOH soln. (80% yield) see (6); from phenol (1:1420) with Cl_2 (2 moles) diluted with CO_2 in AcOH and under these cond. giving exclusively C̄ see (7).]

[For formn. of $\bar{C}$ (together with other prods.) from phenol (1:1420) with Cl_2 (2 moles) (2) (1) (4) (10), with Cl_2 (2 moles) in alk. soln. (11) (12), with *N,N'*-dichlorourea in HCl soln. (13), or with SO_2Cl_2 (14) see indic. refs.; for formn. of $\bar{C}$ from salicylic acid (1:0780) in excess aq. KOH with Cl_2 see (15); from 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichlorosalicylic acid) (3:4935) on distn. with lime see (16) (17); from 2,6-dichloro-3-hydroxybenzaldehyde (3:4160) in excess 50% aq. KOH on htg. at 80° (94% yield) see (5).]

Nuclear substitution of $\bar{C}$. $\bar{C}$ in AcOH with Br_2 (1 mole) (7) (18), or in 50% AcOH with Br_2 (1 mole) in AcOH (19), yields 6-bromo-2,4-dichlorophenol, ndls. from C_6H_6 or lt. pet., m.p. 68–69° (19), 68° (7) (18), b.p. 268° dec. (18), 204° at 19 mm. (19), 198° at 15 mm. (19), 192° at 12 mm. (19) (corresp. methyl ether, m.p. 65° (7); corresp. 2,4-dinitrophenyl ether, yel. lfts. from alc., m.p. 140–141° (19); corresp. *p*-toluenesulfonate, m.p. 82–83° (19)). — [This 6-bromo-2,4-dichlorophenol with excess Br_2 in pres. of Fe powder and absence of aq. yields (20) 2,4-dichloro-3,5,6-tribromophenol, cryst. from AcOH, m.p. 209° (20) (corresp. methyl ether, m.p. 143–144° (20), corresp. benzoate, m.p. 202° (20)).]

$\bar{C}$ in aq. NaOH with I_2 (1 mole) in aq. KI yields (7) 2,4-dichloro-6-iodophenol, ndls. from dil. alc , m.p. 63° (7) (corresp. methyl ether, m.p. 35°, b.p. 278–285° u.c. (7)).

$\bar{C}$ on nitration by soln. in cold fumg. HNO_3, subsequently poured into aq. (4) cf. (21), yields 2,4-dichloro-6-nitrophenol [Beil. VI-241, VI_1-(122)], yel. cryst. from alc., m.p. 121–122° (4), 124° (22).

Condensation reactions involving nuclear hydrogens. [$\bar{C}$ with formalin (1:0145) + conc. HCl + conc. H_2SO_4 in pres. of stream of HCl gas at 35–40° (23), or $\bar{C}$ with trioxymethylene + $AcOH/H_2SO_4$ at 50° (24), gives (54% yield (23)) 6,8-dichlorobenzodioxane-1,3, volatile with steam, cryst. from MeOH, m.p. 111° (24), 109–109.5° (23). — $\bar{C}$ with formalin (1:0145) + conc. HCl in stream of HCl gas at 50° for 36 hrs. gives (72% yield (23)) 3,5-dichloro-2-hydroxybenzyl chloride, ndls. from pet. eth., m.p. 82–84° (23); this prod. on hydrol. with aq. at 50° yields (23) 3,5-dichloro-2-hydroxybenzyl alc., ndls. from aq , m.p. 80–81°, also formed as by-product of the dichlorobenzodioxane mentioned above.]

[$\bar{C}$ with methylal (1·0105), methylene diacetate, or methylene (di)iodide in pres. of conc. H_2SO_4 or $ZnCl_2$ (25) or $\bar{C}$ + formalin (1:0145) with $AcOH/H_2SO_4$ (26) yields methylene-*bis*-(2,4-dichlorophenol) (2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenylmethane); for use of this prod. as mothproofing cpd., antiseptic, and seed disinfectant see (25) (26) (27) (28) (29) (30). — Note, however, that $\bar{C}$ (as Na salt) with methylene (di)chloride (3:5020) at 120–140° in s.t. for 6 hrs. gives (24) *bis*-(2,4-dichlorophenoxy)methane, m.p. 98°. — $\bar{C}$ with SCl_2 or S_2Cl_2 + $AlCl_3$ in CS_2 or CCl_4 yields (31) 2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide, m.p. 188°. — For condens. of $\bar{C}$ with benzaldehyde *o*- (or *p*-) sulfonic acids and use of products as mothproofing agts. see e.g. (26).]

[$\bar{C}$ with phthalic anhydride (1:0725) + $AlCl_3$ at 150° for 2 hrs. yields (36) cf. (37) (38) 2-(3',5'-dichloro-2'-hydroxybenzoyl)benzoic acid, colorless lfts. from alc., m.p. 204° cor. (36), which with conc. H_2SO_4 ring-closes to 2,4-dichloro-1-hydroxyanthraquinone, yel. ndls. from C_6H_6, m.p. 242° (36), 241–242° (39). — $\bar{C}$ with 4,5-dichlorophthalic anhydride (3:4830) + fumg. H_2SO_4 + H_3BO_3 at 195° yields (40) 2,6,7-trichloro-1,4-dihydroxyanthraquinone (2,6,7-trichloroquinizarin).]

Reactions of the phenolic group of $\bar{C}$ (see also under Ⓓ below). $\bar{C}$ behaves as a weak acid: $\bar{C}$ is sol. in aq. alk. but largely pptd. by CO_2. — Dissoc. const. at 25° in aq. is $31. \times 10^{-7}$ (41) cf. (42).

[For study of bactericidal prop. of $\bar{C}$ see (43); for use as insecticide in paper see (44); for prepn. and use of metal complexes as antiseptics see (45).]

[$\bar{C}$ with alkali metals gives corresp. alk. 2,4-dichlorophenolates: K 2,4-dichlorophenolate with CO_2 at 140° yields (15) 3,5-dichloro-2-hydroxybenzoic acid (3,5-dichlorosalicylic acid) (3:4935).]

[C̄ with ethyl α-methylacetoacetate (1:1712) + P_2O_5 gives (14.5% yield (46)) 6,8-dichloro-2,3-dimethylchromone [Beil. XVII₁-(177)], ndls. from alc., m p. 141°.]

[C̄ in 20% aq. KOH htd. 2 hrs. at 100° with Me_2SO_4 (22) cf. (1) yields 2,4-dichlorophenyl methyl ether (2,4-dichloroanisole) [Beil. VI-189, VI_1-(103)], b.p. 232–233° cor. at 743 5 mm.; m.p. 27–28° (47). — C̄ with EtI + K_2CO_3 in acetone refluxed 6–8 hrs. gives (90% yield (48)) 2,4-dichlorophenyl ethyl ether (2,4-dichlorophenetole), oil, b.p. 235–236° (48), 236–237° (4) (for study of cleavage of this ether with HBr/AcOH see (48), for study of rate of formation see (49)). — C̄ with allyl bromide + K_2CO_3 in acetone yields (50) allyl 2,4-dichlorophenyl ether, b p. 144–145° at 25 mm. (50).]

—— **2,4-Dichlorophenyl acetate**: oil, b.p. 244–245° (4), 167–168° at 80 mm. (51). [From C̄ with AcCl refluxed 40 min. (86% yield (51)), this ester with $AlCl_3$ at 170° for 40 min. undergoes Fries rearr. giving (75% yield (51)) 3,5-dichloro-2-hydroxyacetophenone, m.p 95–96° (51).]

Ⓓ **2 4-Dichlorophenyl benzoate**: cryst from alc., m.p. 96.5° (5), 96° (1), 97° [Beil. IX-117]. [From C̄ in dil. aq NaOH shaken with BzCl (5) cf. (1)] [For study of nitration of this ester see (6).]

Ⓓ **2,4-Dichlorophenyl *m*-nitrobenzoate**: ndls. from alc., m p. *115–116°* (6). [From C̄ + *m*-nitrobenzoyl chloride in dil. aq. alk.; for study of its nitration see (6).]

—— **2,4-Dichlorophenyl *p*-nitrobenzoate**: unreported.

—— **2,4-Dichlorophenyl 3,5-dinitrobenzoate**: unreported.

—— **2,4-Dichlorophenyl benzenesulfonate**: unreported.

• Ⓓ **2,4-Dichlorophenyl *p*-toluenesulfonate**: pr. from alc., m p. 125° (6).

Ⓓ **2,4-Dichlorophenyl benzyl ether**: pr. from alc., ether, or pet. eth , m p 62° (52), 61–62° (53), 60° (54), 59.0–59.5° (55). [From C̄ + benzyl chloride (3:8535) + NaOEt in hot alc. (53), or from Na salt of C̄ + benzyl chloride in MeOH (55); note, however, that Na salt of C̄ with benzyl chloride in toluene at 160° for 5 hrs. undergoes instead nuclear alkylation yielding (55) 2,4-dichloro-6-benzylphenol (3,5-dichloro-2-hydroxydiphenylmethane), cryst. from pet. eth., m p 77.0–77.5° (55)]

Ⓓ **2,4-Dichlorophenyl *p*-nitrobenzyl ether**: ndls. from ether, m p. 148–150° (53).

Ⓓ **2,4-Dichlorophenyl 2,4-dinitrophenyl ether**: lfts from AcOH, AcOH/EtOH, or EtOH, m.p. 119° (56), 118–119° (6), 118° (57). [From Na or K salt of C̄ + 2,4-dinitrochlorobenzene refluxed in alc. (56) (6) (57).]

Ⓓ **2,4-Dichlorophenoxyacetic acid (3:4095)**: cryst. from C_6H_6, m p. 138° (58), Neut. Eq. = 221 0. [From C̄ + chloroacetic acid in slight excess aq. NaOH, refluxed and then acidified (87% yield (58)); for studies on use of this prod. as plant hormone see (59).]

—— **2,4-Dichlorophenyl *N*-phenylcarbamate**: unreported.

Ⓓ **2,4-Dichlorophenyl *N*(*p*-iodophenyl)carbamate**: m p. 182–183° (61). [From C̄ + *p*-iodobenzazide in hot lgr (61).]

Ⓓ **2,4-Dichlorophenyl *N*-(*p*-bromophenyl)carbamate**: rods from lgr /AcOEt, m p. 169° cor (62) [From C̄ + *p*-bromobenzazide in hot lgr. (62)]

Ⓓ **2,4-Dichlorophenyl *N*-(*p*-nitrophenyl)carbamate**: yel. pl. from lgr./EtOAc, m.p. 205° cor. (62). [From C̄ + *p*-nitrobenzazide in hot lgr. (63).]

Ⓓ **2,4-Dichlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate**: or.-yel. pr. from lgr. or EtOAc, m.p 153° u c., 157° cor. (64). [From C̄ + 3,5-dinitro-4-methylbenzazide in hot lgr (64).]

—— **2,4-Dichlorophenyl *N*-(α-naphthyl)carbamate**: unreported.

Ⓓ **2,4-Dichlorophenyl *N*-(β-naphthyl)carbamate**: pl. from lgr., m p. 162° u c., 166° cor. (65). [From C̄ + β-naphthyl isocyanate (or azide) in hot lgr. (65)]

similarly. — C̄ (1 mole) with salicylic acid (1:0780) in pyridine at −15° (52) or in C_6H_6 with dimethylaniline (63% yield (52)) gives *O*-carbethoxysalicylic acid [Beil. X-69, X_1-(30)], m.p. 95° (other mono-, di-, and polyhydroxy phenolic acids behave similarly); since the carbethoxy groups so introduced may subsequently be removed by hydrolysis, this process has great value as a means of temporary blocking of phenolic groups (for further discussion and many references see (53)).]

[C̄ also reacts with the sodio derivatives and other metallic enolates: e.g., C̄ (1 mole) with ethyl cyanoacetate (2 moles) in abs. alc. + NaOEt (2 moles) gives (54) diethyl cyanomalonate [Beil. II-811, II_1-(321), II_2-(680)], b.p. 138–140° at 14 mm., D_4^{20} = 1.1128, n_D^{20} = 1.4295 (55). — C̄ with diethyl malonate (1:3581) + NaOEt in alc. (56) or C̄ with dry diethyl sodio-malonate (57) directly (58) (59) or in C_6H_6 refluxed for 10 hrs. (60) gives (yields: 50–80% (59), 60–65% (60)) triethyl methane-tricarboxylate (tricarbethoxymethane) [Beil. II-810, II_1-(320), II_2-(680)], m.p. 29°, b.p. 253°; note that this same prod. is also obtained (yields: 88–93% (61), 90% (62), 80% (63)) from C̄ with diethyl malonate (1:3581) in abs. alc. with Mg + trace CCl_4. — C̄ with the Na enolate of ethyl isobutyrate (1:3095) gives (75% yield (64)) diethyl dimethylmalonate [Beil. II-648, II_1-(276), II_2-(572)], b.p. 195–196° at 760 mm. — The reactn. of C̄ with ethyl sodioacetoacetate cannot be discussed here.]

[C̄ with excess RMgX compounds presumably gives first the corresp. esters which by further normal reactn. with more RMgX are converted to tertiary alcohols: e.g., C̄ with EtMgBr (excess) yields (65) triethylcarbinol (1:6218); however, the intermediate ester can often readily be obtd.; e.g., C̄ (1 mole) with *ter*-BuMgCl (1 mole) in dry ether gives (56% yield (66)) ethyl trimethylacetate (ethyl pivalate (1:3117), and other cases are recorded (66); note, however, that with certain types of RMgX cpd. abnormal reactions can occur: e.g., C̄ with benzyl MgCl yields not only the normal tribenzylcarbinol but also (67) ethyl *o*-toluate (1:3862). — C̄ also reacts with the =N—MgX grouping replacing —MgX by —COOEt (sometimes followed by rearrangement): e.g., C̄ + 3,5-dimethylpyrrole-*N*-(magnesyl bromide) gives (57–58% yield (68)) 5-carbethoxy-2,4-dimethylpyrrole.]

C̄ also reacts readily with NH_3, with primary and secondary amines, with amino acids, etc., to replace one of the H's attached to N by the —COOEt group (see also below and under Ⓓ): e.g., C̄ with excess conc. aq. NH_4OH immediately (if delayed, urea is formed) evaporated to dryness gives (3) ethyl carbamate (urethane) [Beil. III-22, III_1-(9), III_2-(19)], very eas. sol. aq., cryst. from abs. alc., dry ether, $CHCl_3$, or C_6H_6, m.p. 48°, b.p. 184°. — [C̄ (1 mole) in ether with 33% aq. $MeNH_2$ soln. (1 mole) + aq. NaOH below 5° as directed (69) gives (88–90% yield (69)) (70) (71) ethyl *N*-methylcarbamate [Beil. IV-64, IV_1-(330), IV_2-(567)], oil, very sol. aq. (69 g. in 100 ml. aq. at 15.5° (72)), b.p.170°. — Countless other, analogous reactns. cannot be cited here.]

[C̄ with hydroxylamine hydrochloride + conc. aq. Na_2CO_3 (73) or with dry K_2CO_3 in ether (74) gives (89.6% yield (74)) *N*-hydroxyurethane (carbethoxyhydroxamic acid) [Beil. III-95, III_2-(77)], oil, very sol. aq.]

C̄ with hydrazine hydrate in alc. refluxed ½ hr. (75) (for starting with hydrazine sulfate see (76)) gives (yields: 100% (76), 90% (75)) diethyl *sym.*-hydrazinedicarboxylate (*sym.*-dicarbethoxyhydrazine) [Beil. III-98, III_1-(46), III_2-(79)], cryst. from hot aq., ndls. from $CHCl_3$, m.p. 130° (75), 131° (76) (note that the half reaction product, viz., ethyl hydrazinemonocarboxylate (*N*-aminourethane) (ethyl carbazinate), is also known (77) (78) but is an oil. — C̄ (1 mole) with urea (2.1 moles) refluxed for 2–3 hrs. gives (62–65% yield (79)) ethyl allophanate (*N*-carbethoxyurea) [Beil. III-69, III_1-(31), III_2-(56)], m.p. 192°.

C̄ (1 mole) in ether with phenylhydrazine (2 moles) in ether (80) (81) (82) (76) or in aq. pyridine (83) gives (yields: 60–65% (80), 60% (76)) ethyl ω-phenylcarbazinate (*β*-carb-

C̄ has strong lachrymatory properties. — [For study of toxicity see (11).] — C̄ is comml. chemical in U.S.A.

[For prepn. of C̄ from carbonyl chloride (phosgene) (3:5000) with abs. EtOH (1:6130) (90% yield (12)) in pres. of *dimethylaniline, quinoline, or antipyrine (13) or even* $Ca(OH)_2$ (14) see indic. refs.; for formn. of C̄ from diethyl carbonate (1:3150) with PCl_5 (15), from diethyl pyrocarbonate $O(COOEt)_2$ (16) with $SOCl_2$ (17); from pentachloroethyl chloroformate [Beil. III-13, III_1-(6)] (18) or *bis*-(trichloromethyl) carbonate (triphosgene) (3:1915) (19) or *bis*-(trichloromethyl) oxalate [Beil. III-17] (20) with EtOH, or from K xanthate, ethyl xanthate, or benzyl xanthate with Cl_2 + aq. in cold (21) see indic. refs.]

Pyrolysis of C̄. C̄ on htg at 250° decomposes yielding (4) EtCl (3:7015) + CO_2 (for study of this reactn. see (22) (23)); in pres. of certain hydrocarbons or esters (24) or in pres. of *dimethylaniline (25) temp. of this decomposition is lowered to 150°*, in pres. of quinoline to 59° (26) (27), in pres. of $AlCl_3$ to room temp. (28) (see also below under C̄ + pyridine or quinoline).

C̄ in pres. of anhydrous $ZnCl_2$ (29) (30) or even metallic Zn (31) decomposes at room temp. yielding (29) (30) EtCl (3:7015) + ethylene + CO_2 + HCl.

Reactions of the —$COOC_2H_5$ group of C̄. C̄ on hydrolysis, e.g., by boilg. with aq. or dil. acid (32), yields CO_2 + HCl + ethylene; on alkaline hydrolysis, however, no ethylene is formed (32); note that C̄ does not react with cold aq. very rapidly and may even be washed with it to remove alcohol.

[C̄ at its b.p. treated with Cl_2 in sunlight undergoes further substitution by halogen yielding as final prod. (33) (34) pentachloroethyl chloroformate (ref. given above under prepn. of C̄).]

[C̄ with $EtHSO_4$ at 100° under reflux for 6–8 hrs. gives (40% yield (48)) Et_2SO_4 + EtCl (3:7015).]

Reactions of the chlorine atom of C̄. [C̄ on reduction with 3% Na/Hg + aq. gives (51% yield (35)) salt of formic acid (1:1005).]

[C̄ in $CHCl_3$ with Na_2O_2 does not react until 1–2 drops of aq. are added; vigorous actn. then ensues with formn. of the expected (but very explosive) dicarbethoxy peroxide (EtOOC—O—O—COOEt) (36).]

[C̄ with NaSH (37) or with C_2H_5—S—MgBr (38 in ether gives (68% yield (38)) *O,S*-diethyl thiocarbonate [Beil. III-133, III_1-(62), III_2-(105)], b.p. 158–159° cor.; C̄ (2 moles) + aq. (39) or alc. (40) Na_2S, C̄ with BrMgSH in ether (41), or C̄ with aq. potassium trithiocarbonate (39), gives *diethyl thiodiformate (dicarbethoxy sulfide) [Beil. III-133, III_2-(105)]*, b.p. 180° dec.]

[C̄ with thallous fluoride 12 hrs. at room temp., then refluxed 2–3 hrs., gives (47% yield (42)) ethyl fluoroformate, lachrymatory oil, b.p. 57° (42).]

[For rate of reactn. of C̄ with KI in acetone at 25° see (43).]

[C̄ with aq. alc. KCN at −13° (44) or with solid NaCN (contg. 0.2–7.0% moisture) at not above 90° (45) gives (yields: 90% (45), 46% (44)) ethyl cyanoformate [Beil. II-547, II_1-(238), II_2-(510)], b.p. 115–116° (46), D_4^{20} = 1.0034 (47), n_D^{20} = 1.3821 (47).]

C̄ as carbethoxylating agent. C̄ is widely employed as a means of introducing the —COOEt group into other organic molecules by reactn. of the chlorine atom with the H of the alcoholic, phenolic, or enolic OH groups (or their metallic alcoholates, phenolates, enolates, etc.); under appropriate conditions C̄ is also *employed to introduce the —COOEt* group into an aromatic nucleus. Examples of these reactns. are cited below.

[C̄ with NaOMe yields (49) ethyl methyl carbonate [Beil. III-4, III_1-(4)], b.p. 109°. C̄ *with NaOEt yields diethyl carbonate (1:3150); other alcohols behave similarly (50).* — C̄ with K phenolate or C̄ with phenol in ether + dry K_2CO_3 gives (71% yield (51)) ethyl phenyl carbonate [Beil. VI-157], b.p. 229°; other mono-, di-, and polyhydric phenols behave

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(31) Geuther, *J. prakt. Chem.* (2) **6**, 161 (Note) (1872). (32) Thiele, Dent, *Ann.* **302**, 256–257 (1898). (33) Müller, *Ann.* **258**, 50–66 (1890). (34) Anschütz, Emery, *Ann.* **273**, 61–63 (1893). (35) Geuther, *Ann.* **205**, 223–226 (1880). (36) Wieland, von Hove, Börner, *Ann.* **446**, 46–47 (1926). (37) Salomon, *J. prakt. Chem.* (2) **6**, 435–439 (1872). (38) Hepworth, Clapham, *J. Chem. Soc.* **119**, 1195 (1921). (39) Holmberg, *J. prakt. Chem.* (2) **71**, 278–279 (1905). (40) Meyer, *Ber.* **2**, 298 (1869).

(41) Mingoia, *Gazz. chim. ital.* **55**, 719 (1925). (42) Goswami, Sarkar, *J. Indian Chem. Soc.* **10**, 537–539 (1933). (43) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* **47**, 489 (1925); Conant, Kirner, *J. Am. Chem. Soc.* **46**, 249 (1924). (44) Nef, *Ann.* **287**, 308 (1895). (45) Gluud, Nüssler, Keller (to Gesellschaft für Kohlentechnik), Ger. 592,539, Feb. 17, 1934; *Cent.* **1934**, II 3137; *C.A.* **28**, 3117 (1934). (46) Weddige, *J. prakt. Chem.* (2) **10**, 197–199 (1874). (47) Haller, Muller, *Ann. chim.* (8) **14**, 135 (1908). (48) Kraft, Lyutina, *J. Gen. Chem. (U.S.S.R.)* **1**, 190–192 (1931); *Cent.* **1931**, II 3197; *C.A.* **26**, 2167 (1932). (49) Schreiner, *J. prakt. Chem.* (2) **22**, 354 (1880). (50) Rose, *Ann.* **205**, 211–216 (1880).

(51) Claisen, *Ber.* **27**, 3183 (1894). (52) Einhorn, *Ber.* **44**, 435–436 (1911). (53) Meyer, "Analyse und Konstitutionsermittlung organischer Vergindungen," 6th ed., pp. 448–451, 507 (1938). (54) Haller, *Ann. chim.* (6) **16**, 428–429 (1889). (55) Mignonac, Rambeck, *Compt. rend.* **188**, 1299 (1929). (56) Conrad, Guthzeit, *Ann.* **214**, 31–33 (1882). (57) Adickes, *Ber.* **59**, 2527–2528 (1926). (58) Michael, *J. prakt. Chem.* (2) **37**, 476 (1888). (59) Philippi, Hanusch, von Wacek, *Ber.* **54**, 901 (1921). (60) Adickes, Brunnert, Lücker, *J. prakt. Chem.* (2) **130**, 163–166 (1931).

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(71) von Pechmann, *Ber.* **28**, 855–856 [illegible] *Ber.* **27**, 1255 (1894). (74) Jones, *Am.* [illegible]

[illegible] (82) Pieroni, Giannini, *Gazz. chim. ital.* **54**, 170 (1924). (83) Busch, Heinrichs, *Ber.* **33**, 458 (1900). (84) Longo, *Gazz. chim. ital.* **63**, 467–468 (1933); *Cent.* **1933**, II 3115; *C.A.* **28**, 122 (1934). (85) Hopkins, *J. Chem. Soc.* **117**, 278–282 (1920). (86) Wilm, Wischin, *Ann.* **147**, 157–163 (1868). (87) Schmidt, *Z. physik. Chem.* **58**, 516 (1907). (88) Hofmann, *Ber.* **3**, 656 (1870). (89) Dermer, King, *J. Org. Chem.* **8**, 168–173 (1943). (90) Hantzsch, *Ber.* **31**, 180 (1898).

(91) Vles, *Rec. trav. chim.* **53**, 961–966 (1934). (92) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409 (1934). (93) Dixon, Kennedy, *J. Chem. Soc.* **117**, 80–84 (1920). (94) Levy, Campbell, *J. Chem. Soc.* **1939**, 1443.

ethoxy-phenylhydrazine) [Beil. XV-286, XV₁-(71)], cryst. from dil. alc. or C_6H_6/lgr. as monohydrate, m.p. 85° (81) (82), anhydrous form, m.p. 82–83° (81), 80–82° (76). — C̄ with p-nitrophenylhydrazine in pyridine gives (84) β-carbethoxy-p-nitrophenylhydrazine, cryst. from alc., m.p. 198–199° (84). — C̄ with 2,4-dinitrophenylhydrazine in pyridine gives (84) β-carbethoxy-2,4-dinitrophenylhydrazine, cryst. from aq. alc., m.p. 168–169° (64).

C̄ (1 mole) with pyridine (1 mole) in the cold gives first a colorless addn. prod. (85) which rapidly turns red (can be used as test for pyridine (85)) and on warming rapidly decomposes with evolution of CO_2 + EtCl (3:7015); C̄ similarly treated with quinoline gives a yellow amorphous solid, considerably more stable than the above pyridine cpd., but at 100° decomposing similarly but more slowly (85) in the same manner (see also above under pyrolysis).

Ⓓ **Ethyl N-phenylcarbamate (phenylurethane):** ndls. from hot aq., tbls. from 90% alc., m.p. 51.5–52° (86), 51–52° (21) [From C̄ (1 mole) with aniline (2 moles) (86) (21) or from C̄ with aniline + cold aq Na_2CO_3 (87).] [For study of rate of this reactn. see (91).]

Ⓓ **Ethyl N-(p-tolyl)carbamate (p-tolylurethane):** pr. from alc., m.p. 52–53° (21), 52° (88). [From C̄ (1 mole) with p-toluidine (2 moles) in ether (21) (88).]

Ⓓ **N,N'-bis-(Benzyl)urea:** ndls. from alc., m.p. 167.5–169° cor. (89). [From C̄ (1 ml.) with benzylamine (3 ml.) + trace NH_4Cl refluxed 1 hr. (89); note that in this reactn. (unlike the two preceding cases) the reagent amine not only reacts with the chlorine atom of C̄ but *also* ammonolyzes the carbethoxy group; the prod. is therefore a disubstituted urea rather than the ethyl N-benzylcarbamate [Beil. XII-1049], lfts. from lgr., m.p. 48–49° (90), which is formed from C̄ + benzylamine + cold aq. NaOH (90).]

—— **N-(Carbethoxy)phthalimide:** unreported.

—— **N-(Carbethoxy)-3-nitrophthalimide:** unreported.

—— **N-(Carbethoxy)-tetrachlorophthalimide:** unreported. [Note that C̄ with K tetrachlorophthalimide fails to react under reflux and explodes on htg. in s.t. (92).]

—— **S-(Carbethoxy)isothiourea picrate:** m.p. 150–151° (93). [Note that C̄ (1 mole) with thiourea (1 mole) in conc. aq. soln. on treatment with $NaHCO_3$ in slight excess evolves CO_2 and ppts. S-(carbethoxy)isothiourea bicarbonate, bulky white ppt., insol. aq., m.p. 59–60° dec.; this ppt. on *immediate* treatment with dil. HCl dissolves and from the solution PkOH gives S-(carbethoxy)isothiourea picrate; the same prod. may also be obtd. from the original aq. soln. of C̄ + thiourea by direct addn. of PkOH (93). — Note, however, that the above bicarbonate on stdg. with aq. changes spontaneously to N,N-dicarbethoxythiourea, m.p. 97° dec., + thiourea. — Note, however, that C̄ (1 g.) with thiourea (1 g.) in EtOH (10 ml.) refluxed 30 min., then treated with PkOH (1 g.) does *not* yield the above prods. but instead (94) S-ethyl-isothiourea picrate, m.p. 187° (94).]

3:7295 (1) Timmermans, *Bull. soc. chim. Belg.* **31**, 392 (1922). (2) Perkin, *J. Chem. Soc.* **65**, 420 (1894). (3) Dumas, *Ann. chim.* (2) **54**, 225–237 (1833); *Ann.* **10**, 277–288 (1834). (4) Pavlevski, *Ber.* **25**, 1419–1451 (1892). (5) Forster, Newman, *J. Chem. Soc.* **97**, 2573 (1910). (6) Karvonen, *Ann. Acad. Sci. Fennicae* **A-10**, No 4, 19; *Cent.* **1919**, III 808. (7) Mizushima, Kubo, *Bull. Chem. Soc. Japan* **13**, 178 (1938). (8) Guye, Mallet, *Arch. sci. phys. Nat. Genève* (4) **13**, 274–296; *Cent.* **1902**, I 1315. (9) von Auwers, *Ber.* **60**, 2140 (1927). (10) Jaeger, *Z. anorg. allgem. Chem.* **101**, 67 (1917).

1901; *Cent.* **1901**, I 428.

3:7305 α-CHLOROETHYL ETHYL ETHER (α-Chlorodiethyl ether; α-ethoxyethyl chloride)

$CH_3\overset{H}{\underset{Cl}{C}}.O.C_2H_5$ C_4H_9OCl

Beil. I - 606
I_1-(327)
I_2—

B.P. 97.5° cor. at 760 mm. (1)	D_4^{20} = 0.9537 (1)	n_D^{20} = 1.3950 (1)
93–94° at 735 mm. (2)	0.9655 (3)	1.4052 (3)

Colorless liq. which fumes in moist air.

[For prepn. (94% yield (1); 69% yield (6)) from paraldehyde (1:0170) + ethyl alc. (1:6130) + dry HCl see (1) (4); for prepn. (78% yield (5)) from acetaldehyde (1:0100) + ethyl alc. (1:6130) + dry HCl see (2) (5).]

C̄ on stdg. polymerizes to dark tarry residue (1).

[C̄ on bromination yields α,β-dibromoethyl ethyl ether (6) (7)(5).]

C̄ on shaking with aq. yields acetaldehyde (1:0100), ethyl alc. (1:6130), + HCl; for study of rate of hydrolysis see (8).

3:7305 (1) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077–4079 (1931). (2) Mohler, Sorge, *Helv. Chim. Acta* **23**, 1209 (1940). (3) Waterman, de Kok, Leendertse, Schoenmaker, *Rec. trav. chim.* **56**, 437–441 (1937). (4) de Kok, Leendertse, Waterman, *Chem. Weekblad*, **37**, 579–583 (1940); *C.A.* **36**, 4800 (1942). (5) Sherrill, Walter, *J. Am. Chem. Soc.* **58**, 743 (1936). (6) Swallen, Boord, *J. Am. Chem. Soc.* **52**, 654 (1930). (7) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* **52**, 3400 (1930). (8) Mohler, Hartnagel, *Helv. Chim. Acta* **25**, 859–863 (1942); *C.A.* **37**, 1799 (1943).

3:7325 *d,l*-2-CHLOROPENTANE (*sec.*-(2)Amyl chloride; methyl-*n*-propylcarbinyl chloride)

$CH_3.CH_2.CH_2—\overset{H}{\underset{Cl}{C}}—CH_3$ $C_5H_{11}Cl$

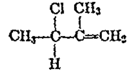
Beil. I - 131
I_1-(43)
I_2-(95)

B.P.			F.P.	
97°	at 770 mm.	(16)	−139 to −137° (1)	D_4^{20} = 0.8732 (16)
96.84–96.88°	at 760 mm.	(1)		0.8695 (1)
96.6–96.8°	at 760 mm.	(2)		
96.87–96.96°	at 759 mm.	(5)		n_D^{20} = 1.40791 (16)
96.7°	at 760 mm.	(14)		1.4069 (1)
95.9–96.6°		(3)		1.4068 (4)
95.5–96.0°	at 755 mm.	(4)		
95°	at 729 mm.	(1)		

Note that all samples of C̄ reported prior to 1935 were undoubtedly mixts. of 2-chloropentane (C̄) with 3-chloropentane (3:7330). Each of these cpds. is with great ease partially converted to the other (see text), and their mixt. cannot be separated by fractional distillation (1).

[For prepn. of C̄ (or its mixt. with 3-chloropentane (3:7330)) from pentanol-2 (1:6185) with conc. HCl on long stdg. at room temp. (78% yield (1)) or in s.t. at 110° (3) see (1) (2) (3); with conc. HCl + $ZnCl_2$ (yield: 70% (6), 49% (16)) see indic. refs.; with PCl_3 + $ZnCl_2$ (64% yield (6)) or PCl_5 + $ZnCl_2$ (56% yield (6)) see (6); with $SOCl_2$ + pyridine (gives least rearr. (1)) (yield: 28% (1), 67% (6)) see (1) (6); from pentene-2 on shaking 10 hrs. at room temp. with conc. HCl see (5) (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane (C̄) and 3-chloropentane (3:7330) (1).] [For formn. of C̄ in small amt. during reactn. of pentanol-1 (1:6205) with HCl + $ZnCl_2$ see (15).]

3:7300 *d,l*-3-CHLORO-2-METHYLBUTENE-1 C_5H_9Cl Beil. I - 211
(α,β-Dimethylallyl chloride) I_1-(87)
I_2--



B.P. 93.8° at 760 mm. (1) $D_4^{20} = 0.9088$ (1) $n_D^{20} = 1.4304$ (1)
18.0–18.1° at 30 mm. (1)

Note: C̄ by virtue of facile allylic transposition is in equilibrium with its synionic isomer, 1-chloro-2-methylbutene-2 (3:7485); reactns. of C̄ may therefore yield also derivatives related to its isomer.

[For prepn. of C̄ (or its mixt. with 1-chloro-2-methylbutene-2) by actn. of Cl_2 as specified (1) on "*tertiary amylene*" (*a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with* some 2-methylbutene-1 (1:8210)) see (1). — The relative amt. of C̄ and its isomer is not constant but usually is about 60% of C̄ with 40% of 1-chloro-2-methylbutene-2, the ratio, however, being independent of the proportion of the two olefins in the starting material.]

[For formn. of C̄ from 2-methylbutene-2 (1:8220) with Cl_2 see (2); from 2-methylbutene-1 (1:8210) see (3); from 2,3-dichloro-2-methylbutane (3:7975) + alc. KOH (3) or by thermal dehydrohalogenation at 420–450° (4) see indic. refs.]

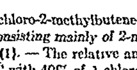
C̄ on hydrolysis gives not only the corresponding alc. but also that corresponding to the isomeric 1-chloro-2-methylbutene-2 (3:7485) together with a little isopropyl methyl ketone. For details see the isomer (3:7485).

C̄ with HCl yields (2) 2,3-dichloro-2-methylbutane (3:7975) + 1,3-dichloro-2-methylbutane (3:9228).

C̄ adds Br_2 giving (3) 1,2-dibromo-3-chloro-2-methylbutane, m.p. 197–198° (3).

3:7300 (1) Burgin, Engs, Groll, Hearne, *Ind Eng Chem* **31**, 1416–1417 (1939). (2) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936), *Cent.* **1937**, I 572; *C.A.* **31**, 1003 (1937). (3) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1062–1067 (1938), *Cent* **1939**, II 4221; *C.A.* **33**, 3755 (1939) (4) Due, Muessig (to Standard Oil Development Co) U.S. 2,332,778, Oct. 26, 1943, *C.A.* **38**, 1750 (1944).

3:7303 1-CHLORO-2-METHYLBUTENE-1 C_5H_9Cl Beil. I —
I_1—
I_2-(187)



B.P. 96–97° (1) $D_4^{20} = 0.9170$ (1)

Oil with agreeable odor. — Insol. aq., sol. ether.

[For prepn. of C̄ from 1-chloro-2-methylbutanol-2 (3:8175) by loss of H_2O on distn. with anhyd. oxalic acid (1:0535) (11% yield (1) together with other prods.), or on treatment with PCl_5 (2) or Ac_2O + trace conc. H_2SO_4 (2) see indic. refs.; for formn. of C̄ from 2-methylbutanediol-1,2 with PCl_5 (2) or from 1,2-epoxy-2-methylbutane (α-ethyl-α-methylethylene oxide) with PCl_5 (1 mole) in cold (1) (2) or with $SOCl_2$ (2) see indic. refs.]

[C̄ with PCl_5 adds Cl_2 yielding (2) a cpd. $C_5H_9Cl_3$, b.p. 180–184°.]

C̄ adds Br_2 readily (2).

[For behavior of C̄ with NaI in acetone see (1).]

3:7303 (1) Chalmers, *Trans Roy Soc. Can.* (3) **22**, III 75–78 (1928); *Cent.* **1929**, I 631–632; *C.A.* **23**, 2694 (1929). (2) Seyer, Chalmers, *Trans Roy Soc. Can* (3) **20**, III 337–339 (1926); *Cent.* **1927**, II 1811, *C.A.* **21**, 2663 (1927).

$\bar{C}$ is stable (no change in n_D^{20}) on htg. in s.t. at 100° for 48 hrs. (1). —However, $\bar{C}$ on shaking at 26–28° for 24 hrs. with $HCl + ZnCl_2$ gives a mixt. consisting of 20% $\bar{C}$ + 80% 2-chloropentane (1).

[For study of rate of hydrolysis by water at 80° and 180° and rate of cleavage of HCl at 180° see (12).]

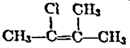
- Ⓓ Diethylacetanilide: $\bar{C}$ with Mg in dry ether yields R.Mg.Cl which, upon reactn. with phenyl isocyanate and subsequent hydrolysis, yields (1) (3) (4) (5) diethylacetanilide, m.p. 127.5° (8), 126.8° (9), 126–127° (5), 125–128° (1), 123–124° cor. (10), 122° (3), 121° (11). [For m.p./compn. data and diagrams for mixts. of diethylacetanilide (from $\bar{C}$) with methyl-*n*-propylacetanilide (from 2-chloropentane) see (4) (3) (11)] [For crystallographic study of these two anilides see (13).]
- Ⓓ Diethylacet-*p*-toluidide: m.p. 107.5–108.5° u.c. (5), 116.2° (9).
- Ⓓ Diethylacet-α-naphthalide: m.p. 117–118° u.c. (5).

3:7330 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2536–2538 (1938). (2) Hass, *J. Chem. Education* **13**, 493 (1936). (3) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* **7**, 231–233 (1935). (4) Kharasch, Walling, Mayo, *J. Am. Chem. Soc.* **61**, 1559–1564 (1939). (5) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117–2120 (1934). (6) Koelsch, McElvain, *J. Am. Chem. Soc.* **52**, 1164–1169 (1930). (7) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (8) Tiffeneau, *Compt. rend.* **204**, 592 (1937). (9) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933). (10) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1065 (1931).

(11) Lauer, Stodola, *J. Am. Chem. Soc.* **56**, 1218 (1934). (12) Ayres, *Ind. Eng. Chem.* **21**, 899–904 (1929). (13) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* **60**, 2541 (1938). (14) Vogel, *J. Chem. Soc.* **1943**, 638, 640.

3:7335 3-CHLORO-2-METHYLBUTENE-2 C_5H_9Cl Beil. I - 213

(Trimethylvinyl chloride) I_1— I_2-(189)



B.P.			
97–98° (1)	D_4^{20} = 0.9096 (5)		n_D^{20} = 1.4320 (5)
96–99° (2)			1.4380 (3)
94–99° (3)	D_4^{20} = 0.925 (3)		
94° at 748 mm. (4)			
91–92° at 741 mm. (5)	D_0^{18} = 0.9215 (1)		

[For prepn. of $\bar{C}$ from isopropyl methyl ketone (1:5410) with PCl_5 see (3) (4); from 3-chloro-2-methylbutanol-2 (3:8030) by dehydration with P_2O_5 (50% yield (1)), anhyd. oxalic acid (6) at 130°, or strong oxygenated mineral acids such as H_2SO_4 (92% yield (7)) see indic. refs.]

[For formn. of $\bar{C}$ (together with other prods.) from 2,3,3-trichloro-2-methylbutane (3:4755) (8) or from 2,3-dichloro-2-methylbutane (3:7975) with alc. KOH (2), from 2-methylbutene-2 (1:8210) with $Cl_2 + NaHCO_3$ at 0° (70–80% yield (9)) or with *ter*-butyl hypochlorite (3:7165) (47.5% yield (5)), or from 2-methylbutanol-2 (1:6160) with Cl_2 (10) see indic. refs.]

$\bar{C}$ with $Cl_2 + NaHCO_3$ at 0° gives (9) 80% 3,3-dichloro-2-methylbutene-1 (3:7690) + 10% addn. prod. 2,3,3-trichloro-2-methylbutane (3:4755).

$\bar{C}$ in cold ether adds Br_2 giving (1) (2) 2,3-dibromo-3-chloro-2-methylbutane, cryst. m.p. 197° (1), 197–198° (2).

3:7335 (1) Krassuskiĭ, *J. Russ Phys.-Chem. Soc.* **33**, 15–17 (1901); *Cent.* **1901**, I 995. (2) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1062–1067 (1938); *Cent.* **1939**, II 4221; *C.A.* **33**, 3755 (1939). (3) Gredy, *Bull. soc. chim.* (5) **2**, 1951 (1935). (4) Béhal, *Ann. chim.* (6) **15**, 284–285

C̄ is stable (no change in n_D^{20}) on htg. in s.t. at 100° for 48° (1). — However, C̄ on shaking at 26–28° for 24 hrs. with HCl + $ZnCl_2$ gives a mixt. consisting of 80% C̄ + 20% 3-chloropentane (3:7330) (1).

[For study of rate of hydrolysis by water at 80° and 180° see (7); for rate of reactn. with KI in acetone at 60° see (8); for reactn. with Na see (9).]

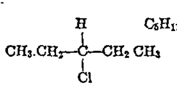
Ⓓ Methyl-*n*-propyl-acetanilide: C̄ with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (1) (2) (4) (10) methyl-*n*-propyl-acetanilide, m.p. 94–96° (1), 95.2° (11), 92.6° (12), 92.5° (2), 88° cor. (13). [For m.p./compn. data and diagrams for mixts. of methyl-*n*-propyl-acetanilide (from C̄) with diethylacetanilide (from 3-chloropentane) see (4) (2) (12).] [For crystallographic study of these two anilides see (15).]

Ⓓ Methyl-*n*-propyl-acet-*p*-toluidide: m.p. 90–92° u.c. (10); 80.5° (11).

Ⓓ Methyl-*n*-propyl-acet-α-naphthalide: m.p. 102.5–103.5° (10).

3:7325 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2536–2538 (1938). (2) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* **7**, 231–233 (1935). (3) Kohlrausch, Köppl, *Monatsh.* **65**, 195 (1935). (4) Kharasch, Walling, Mayo, *J. Am. Chem. Soc.* **61**, 1559–1564 (1939). (5) Norris, Reuter, *J. Am. Chem. Soc.* **49**, 2630–2631 (1927). (6) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (7) Ayres, *Ind. Eng. Chem.* **21**, 899–904 (1929). (8) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (9) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 757 (1936). (10) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117–2120 (1934).
(11) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933). (12) Lauer, Stodola, *J. Am. Chem. Soc.* **56**, 1218 (1934). (13) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1065 (1931). (14) Hass, *J. Chem. Education* **13**, 492–493 (1936). (15) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* **60**, 2541 (1938). (16) Vogel, *J. Chem. Soc.* **1943**, 638, 640.

3:7330 3-CHLOROPENTANE
(*sec.*-(3)Amyl chloride; diethylcarbinyl chloride)



$C_5H_{11}Cl$ Beil. I - 131, I_1—, I_2-(95)

B.P.			F.P.		
97.76–97.82°	at 760 mm.	(1)	−105 to −106° (1)	D_4^{20} = 0.8795	(1)
97.3°	at 760 mm.	(2)		0.8723	(14)
97.1–97.4°	at 760 mm.	(3)			
96.8–97.2°	at 755 mm.	(4)		n_D^{20} = 1.4104	(1)
96.7–97.1°	at 758 mm.	(5)		1.4103	(4)
96°	at 753 mm.	(14)		1.40820	(14)
96–97°	at 729 mm.	(6)			

Note that all samples of C̄ reported prior to 1935 were undoubtedly mixts. of 3-chloropentane (C̄) with 2-chloropentane (3:7325). Each of these cpds. is with great ease partially converted to the other (see text), and the mixture cannot be separated by fractional distillation (1).

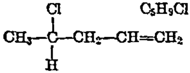
[For prepn. of C̄ (or its mixture with 2-chloropentane (3:7325)) from pentanol-3 (1:6175) with conc. HCl on long stdg. at room temp. (yield: 84% (1); 69% (3)) see (1) (3); with dil. HCl see (5); with conc. HCl + [illegible]
with PCl_3 + $ZnCl_2$ (60% yield [illegible]
pyridine (gives least rearr. (1))
(1:8215) + HCl in presence of $FeCl_3$ or AcOH see (4).] [Note that both pentanol-2 (1:6185) and pentanol-3 (1:6175) with HCl even at room temp. give mixts. of 2-chloropentane (3:7325) and 3-chloropentane (C̄) (1).] [For formn. of C̄ in small amt. during reactn. of pentanol-1 (1:6205) with HCl + $ZnCl_2$ see (12).]

For anal. of mixts. of C̄ with 1-chloro-3-methylbutane (3:7365) via rate of reactn. with KI in acetone see (2).

C̄ with Mg in dry ether does not react (8). [However, from corresp. *d,l-sec.*-butylcarbinyl *bromide* the R.Mg.Br cpd. was obtd. (9) in 66% yield and with phenyl isocyanate yielded *N*-(*sec.*-butylacet)anilide, m.p. 88° cor. (9), 87° (10).]

3:7345 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* **27**, 1192–1195 (1935). (2) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.* **7**, 231–233 (1935). (3) Kohlrausch, Köppl, *Monatsh.* **65**, 195 (1935). (4) Ayres, *Ind. Eng. Chem.* **21**, 900 (1929). (5) Brauns, *J. Research Natl. Bur. Standards* **18**, 323–324, 327–328 (1937). (6) Whitmore, Olewine, *J. Am. Chem. Soc.* **60**, 2570–2571 (1938). (7) Brown, Kharasch, Chao, *J. Am. Chem. Soc.* **62**, 3439 (1940). (8) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117 (1934). (9) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1063–1068 (1931). (10) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933).
(11) Brown, Groot, *J. Am. Chem. Soc.* **64**, 2566 (1942).

3:7350 *d,l*-4-CHLOROPENTENE-1 C_5H_9Cl Beil. I —
I_1-(86)
I_2—



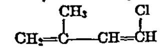
B.P. 97–100° (1) **$D^{15}_{-} = 0.934$ (1)** **$n^{15}_{D} = 1.417$ (1)**

The levorotatory form of C̄ has $D^{25}_{4} = 0.8794$ (2), $n^{25}_{D} = 1.4218$ (2), but no b.p. or method of prepn. is recorded.

[For prepn. of C̄ from penten-1-ol-4 (allyl-methyl-carbinol) [Beil. I-443] with PCl_5 at 0° see (1).]

3:7350 (1) Pariselle, *Compt. rend.* **154**, 712 (1912). (2) Levene, Rothen, *J. Chem. Phys.* **5**, 982 (1937).

3:7355 1-CHLORO-3-METHYLBUTADIENE-1,3 C_5H_7Cl Beil. S.N. 12
(4-Chloro-2-methylbutadiene-1,3)



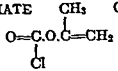
B.P. 99–100° (1)
97.5–98° (2)
$D^{20}_{4} = 0.9543$ (1) (2) **$n_{\alpha}^{-} = 1.47189$ (1)**

[For prepn. of C̄ from 1-chloro-3-methylbutadiene-1,2 (3:7390) by stdg. several days with HCl + Cu_2Cl_2 + NH_4Cl see (2).]

C̄ without solvent on htg. with maleic anhydride (1:0625) evolves HCl and gives (1) a mixt. of 4 acids: 2 dicarboxylic acids, m.p. 210–211° (1) (2) and m.p. 239–241° (1), and 2 tetracarboxylic acids, m.p. 298–299° (1) and m.p. 352–353° (1) (2); with solvent only the acids of m.p. 210–211° and 352–353° are formed (2).

3:7355 (1) Favorskii, Favorskaya, *Compt. rend.* **200**, 839–840 (1935); *Cent.* **1935**, II 1340; *C.A.* **29**, 3651 (1935). (2) Favorskii, Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 386–395 (1939); *C.A.* **33**, 9281 (1939).

3:7358 ISOPROPENYL CHLOROFORMATE $C_4H_5O_2Cl$ Beil. S.N. 19
(Isopropenyl chlorocarbonate)



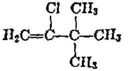
B.P.
at 760 mm. (estimated) (1)
at 746 mm. (1)

$D^{20}_{20} = 1.103$ (1)

10, 381 (1897)

3:7340 2-CHLORO-3,3-DIMETHYLBUTENE-1 $C_6H_{11}Cl$ Beil. I - 218

(3-Chloro-2,2-dimethylbutene-3) I_1— I_2-(195)



B.P. 98° (1)
97–99° (2)

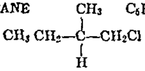
[For prepn. of C̄ from *ter*-butyl methyl ketone (pinacolone) (1:5425) with PCl_5 on htg. (1) (50% yield (3)) or from 3,3-dichloro-2,2-dimethylbutane (3:4325) on htg. with alc. KOH at 150° (1) (3) or with KOAc + phenol (4) see indic. refs.]

C̄ with alc. KOH (3) or htd. at 160–200° for 5 hrs. with powdered KOH (or NaOH (5)) *moistened with alc. (2) gives (80.5% yield (2)) ter-butylacetylene [Beil. I-256]*, b.p. 36.4–37.8° at 768.3 mm. (2).

3:7340 (1) Delacre, *Bull acad. roy. Belg* **1906**, 7–41; *Cent* **1906**, I 1233. (2) Bartlett, Rosen, *J. Am. Chem Soc.* **64**, 544 (1942) (3) Delacre, *Bull soc chim.* (3) **35**, 343–344 (1906). (4) Meerwein, Wortmann, *Ann.* **435**, 194, Note 1 (1924). (5) de Graef, *Bull. soc. chim. Belg.* **34**, 429 (1925).

3:7345 *d,l*-1-CHLORO-2-METHYLBUTANE $C_5H_{11}Cl$ Beil. I - 134

(*d,l-sec.*-Butylcarbinyl chloride) I_1- (46) I_2-(100)



B.P.		D_4^{20} unrecorded (See note below.)	n_D^{20} unrecorded (See note below.)
99.9°	at 760 mm. (1) (2)		
99.8–100°	at 760 mm. (2)		
99.5–100.5°	(3)		
99°	(4)		
52.5°	at 150 mm. (1)		

[Note: for active *d* stereoisomer: b.p. 100.45° at 760 mm (5), 99.5° at 750 mm. (11), *86.8° at 500 mm (5), 80.0° at 400 mm. (5), 71.5° at 300* mm. (5), 60.4° at 200 mm. (5), 43.0° at 100 mm. (5), 27.7° at 50 mm. (5); D_4^{20} 0.8857 (5), 0.8852 (6), n_D^{20} = 1.4124 (5), 1.4125 (6), 1.4126 (11).]

The sepn. of C̄ from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) by fractional distillation cannot be effected (1) (2).

[For prepn. of C̄ from the corresponding alc., *d,l-sec.*-butylcarbinol (cf. 1:6195) with HCl gas at 90° for 6 hrs. (49% yield) see (2); with $SOCl_2$ see (3); for prepn. of *d*-form from corresp. alc. (1:6195) by satn. at 0° with HCl gas and htg. in s.t. 5 hrs. at 100° (20% yield) see (5), by use of $SOCl_2$ + pyridine (yield: 87% (11), 82% (7), 77% (6)) see (6) (7).] — [For formn. by chlorination of crude pentane see (4).]

C̄ *is not hydrolyzed by aq. either at 80° or at 180° (4).* — For rate of loss of HCl at 180° to yield 2-methylbutene-1, b.p. 31° (1:8210), see (4).

3:0560 (1) Holleman, *Rec. trav. chim.* **37**, 96–107 (1918). (2) van de Lande, *Rec. trav. chim.* **51**, 103, 110 (1932). (3) Kohlrausch, Stockmair, Ypsilanti, *Monatsh.* **67**, 89 (1936). (4) Fischer, *Ann. Suppl.* **7**, 180–190 (1870). (5) Lock, *Monatsh.* **55**, 311–312 (1930). (6) Groves, Turner,

(11) Chandelon, *Ber.* **16**, 1751–1752 (1883). (12) Chulkov, Parini, Staroselets, *Org. Chem. Ind.* (*U.S.S.R.*) **3**, 97–101 (1937); *Cent.* **1938**, I 1419; *C.A.* **31**, 4967 (1937). (13) Likhosherstov, *J. Russ. Phys.-Chem. Soc.* **61**, 1019–1023, 1025–1028 (1929); *Cent.* **1930**, I 1294; *C.A.* **24**, 836 (1930). (14) Steinkopf, Mieg, Herold, *Ber.* **53**, 1145 (1920). (15) Tarugi, *Gazz. chim. ital.* **30**, II 489, 491 (1900). (16) Hecht, *Am. Chem. J.* **12**, 505 (1890). (17) Zincke, *Ann.* **261**, 253–254 (1891). (18) Garzino, *Gazz. chim. ital.* **17**, 495–502 (1887). (19) Rox, Turner, *J. Chem. Soc.* **1930**, 1861–1863. (20) Kohn, Dömötör, *Monatsh.* **47**, 215–216 (1926).

(21) Armstrong, *J. Chem. Soc.* **25**, 96 (1872). (22) Kohn, Kramer, *Monatsh.* **49**, 156 (1928). (23) Buehler, Brown, Holbert, Fulmer, Parker, *J. Org. Chem.* **6**, 905–906 (1941). (24) Ziegler, Simmler, *Ber.* **74**, 1871–1879 (1941). (25) Weiler, Wenk, Stötter, Ger. 540,208, Dec. 12, 1931; Brit. 337,832, Dec. 4, 1930; French 39,334, Oct. 12, 1931; *Cent.* **1932**, I 3013. (26) Weiler, Wenk, Stötter, U.S. 1,707,181, March 26, 1929; French 651,646, Feb. 21, 1929; *Cent.* **1929**, II 499. (27) I.G., Austrian 118,640, July 25, 1930; *Cent.* **1930**, II 2978. (28) I.G., Swiss 134,012, Sept. 2, 1929; *Cent.* **1930**, I 1876. (29) I.G., Brit. 334,847, Oct. 9, 1930; *Cent.* **1931**, II 618. (30) I.G., Brit. 337,473, Nov. 27, 1930; *Cent.* **1931**, I 2233.

(31) Muth (to I.G.), Ger. 583,055, Aug. 28, 1933; *Cent.* **1933**, II 3883. (32) I.G., Swiss 137,923–137,929; 138,180–138,183, April 16, 1930; *Cent.* **1930**, II 1453. (33) I.G., Swiss 148,330, Oct. 1, 1931; *Cent.* **1932**, I 1845. (34) Weiler (to I.G.), Ger. 548,822, April 20, 1932; *Cent.* **1932**, II 799. (35) Weiler, Retter (to I.G.), Ger. 604,980, Nov. 3, 1934; *Cent.* **1935**, I 1150. (36) Ullmann, Conzetti, *Ber.* **53**, 827, 831–832 (1920). (37) Scottish Dyes, Ltd. + Thomas + Hooley, Brit. 234,533, June 25, 1925; *Cent.* **1926**, I 245. (38) Ullmann, Ger. 282,493, March 6, 1915; *Cent.* **1915**, I 643. (39) Zahn, *Ber.* **67**, 2078 (1934). (40) Scottish Dyes, Ltd. + Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; *Cent.* **1932**, I 2095.

(41) Hantzsch, *Ber.* **32**, 3070 (1899). (42) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935). (43) Ordal, *Proc. Soc. Exptl. Biol. Med.* **47**, 387–389 (1941); *C.A.* **35**, 6061 (1941). (44) Ellis (to Insulite Co.), U.S. 2,161,654, June 6, 1939; *Cent.* **1939**, II 4620. (45) I.G., Brit. 356,192, Oct. 1, 1931; *Cent.* **1931**, II 3360. (46) Simonis, Schuhmann, *Ber.* **50**, 1148 (1917). (47) Lock, *Monatsh.* **62**, 184–185 (1933). (48) Birosel, *J. Am. Chem. Soc.* **53**, 1408–1412 (1931). (49) Goldsworthy, *J. Chem. Soc.* **1926**, 1254–1256. (50) Raiford, Howland, *J. Am. Chem. Soc.* **53**, 1055 (1931).

(51) Chien, Yin, *J. Chinese Chem. Soc.* **7**, 40–45 (1939); *C.A.* **34**, 1979 (1940). (52) Bradfield, Jones, *J. Chem. Soc.* **1931**, 2906. (53) von Auwers, *Ann.* **357**, 92–93 (1907). (54) Baw, *J. Indian Chem. Soc.* **3**, 104 (1926). (55) Huston, Eldredge, *J. Am. Chem. Soc.* **53**, 2263 (1931). (56) Bost, Nicholson, *J. Am. Chem. Soc.* **57**, 2368–2369 (1935). (57) Raiford, Thiessen, Wernert, *J. Am. Chem. Soc.* **52**, 1208 (1930). (58) Pokorny, *J. Am. Chem. Soc.* **63**, 1768 (1941). (59) Zimmermann, *Ind. Eng. Chem.* **35**, 597–599 (1943). (60) Zimmermann, Hitchcock, *Contrib.*

(62) Sah, Cheng, -599 (1939). (64)

Sah, *Rec. trav. chim.* **58**, 587–589 (1939). (65) Sah, *Rec. trav. chim.* **58**, 454–458 (1939).

Colorless lachrymatory liq. with sharp and unpleasant odor.

[For prepn. of C̄ from acetone (1:5400) with liq. phosgene (3:5000) for ½ hr. at room temp. see (1).]

3:7358 (1) Matuszak, *J. Am. Chem. Soc.* **56**, 2007 (1934).

3:7360 3-CHLOROPENTADIENE-1,3 C_5H_7Cl Beil. S.N. 12

("Methylchloroprene"; pirylene monohydrochloride)

$$CH_3{-}CH{=}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

B.P.			
99.5–101.5° at 759 mm. (1) (2)	D_4^{20} = 0.9576 (1) (2)	n_D^{25} = 1.4745 (3)	
98.5–101° (3)		n_D^{20} = 1.4785 (1) (2)	

Colorless liq. with characteristic odor; after addition of hydroquinone (as antioxidant) can be distilled (1). — [For polymerization of C̄ see (1) (2).]

[For prepn. of C̄ from penten-1-yne-3 (α-methyl-β-vinylacetylene = pirylene (3)) by shaking with conc. *HCl* contg. CuCl + NH_4Cl see (1) (2) (3).]

C̄ on htg. with 1,4-naphthoquinone (1:9040) at 100° for 2 hrs. then treated with alc. NaOH, and aerated (to oxidize the intermediate addn. prod.), gives (1) (3) 2-chloro-1-methylanthraquinone, yel. ndls. from AcOH, m.p. 181° (1), 180.7–181.0° (3). [Dif. from 1-chloro-2-methylbutadiene-1,3 (3:9200) q.v.]

3:7360 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* **55**, 1624–1627 (1933). (2) Jacobson (*to du Pont*), *U S 1,950,440, March 13, 1934; Cent. 1934, II 1037; C.A.* **28**, 3278 (1934). (3) Sargent, Buchman, Farquhar, *J. Am. Chem. Soc.* **64**, 2693 (1942).

3:7365 4-CHLORO-2-METHYLBUTANE $C_5H_{11}Cl$ Beil. I - 135, I_1-(46), I_2-(100)

(Isoamyl chloride; 1-chloro-3-methylbutane)

$$ClCH_2.CH_2{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3$$

B.P.			F.P.		
101°		(1)	−104.4° (6)	D_4^{20} = 0.8927 (7)	n_D^{20} = 1.4096 (7)
100–101°		(2)		0.8732 (25)	1.40909 (25)
99.15°	at 760 mm.	(3)			1.4087 (6)
99°	at 777 mm.	(25)			
98.8°	at 760 mm.	(4) (5)			
98.1°		(6)			

C̄ forms many azeotropes: e.g., C̄ with EtOH (1:6130), b.p. 78.3°, gives a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. 59 wt. % C̄ (8); with *n*-propyl alc. (1:6150), b.p. 97.2°, a const.-boilg. mixt., b.p. 89.4° at 760 mm., contg. 69 wt. % C̄ (8); with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 79.2° at 760 mm., contg. 57 wt. % C̄ (8) with isobutyl alc. (1:6165), b.p. 107.85°, a const.-boilg. mixt., b.p. 94.5° at 760 mm., contg. 78 wt. % C̄ (8). [For still others see Beil. I_2-(101).]

[For p[illegible]

HCl + [illegible]

$ZnCl_2$ [illegible]

(100% [illegible]]

[For study of hydrolysis by aq. at 80° and 180°, loss of HCl at 180°, and *esterification* with NaOAc at 180° see (1).]

[For study of *rate* of reactn. with KI in acetone at 60° see (2); for use in anal. of mixts. of C̄ with 1-chloro-2-methylbutane (3:7345) see (5).]

$\bar{C}$ with Mg in dry ether + trace I_2 gives RMgCl (yield in 5 hrs. 96.3% (26)); this upon oxidation with O_2 yields (17) isoamyl alc. (1:6200) q.v. [Note: for m.p./compn. data for mixts. of *N*-phenylcarbamates of isoamyl alc. (1:6200) and *d,l-sec.*-butylcarbinol (1:6195) see orig. ref. (17).]

- Ⓓ Isocaproanilide: m.p. 112.0° (18) (19); 111.5° (20); 110.5° u.c. (21); 108° cor. (22). [From RMgCl (21) or RMgBr (22) with phenyl isocyanate.]
- Ⓓ Isocapro-*p*-toluidide: m.p. 63.0° (18); 61.5–62.5° u.c. (21). [From RMgCl + *p*-tolyl isocyanate (21).]
- Ⓓ Isocapro-*α*-naphthalide: m.p. 110–111° u.c. (21). [From RMgCl + *α*-naphthyl isocyanate (21).]
- Ⓓ Isoamyl mercuric chloride (RHgCl): m.p. 86° (23).
- Ⓓ *S*-Isoamylisothiourea picrate: m.p. 173° (24). [In poor yield from $\bar{C}$ in alc. on refluxing 2 hrs. with thiourea, followed by addn. of PkOH (24).]
- —— *N*-(Isoamyl)tetrachlorophthalimide: lfts. from EtOH, m p. 170–171° (27).

3:7365 (1) Ayres, *Ind. Eng. Chem.* **21**, 900 (1929). (2) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (3) Timmermans, *Bull. soc. chim. Belg.* **30**, 66 (1921). (4) Hass, McBee, Weber, *Ind. Eng. Chem.* **27**, 1192 (1938). (5) Hass, Weber, *Ind. Eng. Chem., Anal. Ed.*, **7**, 231–233 (1935). (6) Turkevich, Smyth, *J. Am. Chem Soc.* **64**, 737 (1942). (7) Washburn, Keim, *J. Am. Chem. Soc.* **62**, 1747 (1940). (8) Lecat, *Rec trav. chim.* **46**, 242 (1927). (9) Mouneyrat, *Ann. chim.* (7) **20**, 538 (1900). (10) Malbot, *Bull. soc. chim.* (3) **1**, 603 (1889).

(11) Gleditsch, *Bull. soc. chim* (3) **35**, 1094–1095 (1906). (12) Norris, Taylor, *J. Am. Chem. Soc.* **46**, 756 (1924). (13) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (14) Dehn, Davis, *J Am. Chem. Soc.* **29**, 1332 (1907). (15) Cahours, *Ann.* **37**, 164 (1841). (16) Ross, Bibbins, *Ind. Eng. Chem.* **31**, 255–256 (1939). (17) Davydova, Papkina, Tischenko, *J. Gen. Chem.* (*U.S S.R*) **6**, 1615–1623 (1936); *Cent.* **1937**, I 3786. (18) Hommelen, *Bull. soc chim. Belg* **42**, 249 (1933). (19) Brunner, Farmer, *J. Chem. Soc.* **1937**, 1044. (20) Dragendorff, *Ann.* **487**, 76 (1931).

(21) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2119 (1934). (22) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1065 (1931). (23) Marvel, Gauerke, Hill, *J. Am. Chem. Soc.* **47**, 3010 (1925). (24) Levy, Campbell, *J. Chem. Soc.* **1939**, 1443. (25) Vogel, *J. Chem. Soc.* **1943**, 638,640. (26) Houben, Boedler, Fischer, *Ber.* **69**, 1769, 1782 (1936). (27) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934).

3:7370 *n*-BUTYRYL CHLORIDE $CH_3.CH_2.CH_2.\underset{\displaystyle Cl}{\underset{|}{C}}{=}O$ C_4H_7OCl

Beil. II - 274
II_1-(122)
II_2-(251)

B.P.			F.P.		
101.8°	at 760 mm.	(1)	−89.0° (12)	D_{-}^{25} = 1.0154 (2)	
102°		(2)	−89.3° (1)		n_D^{25} = 1.4115 (2)
101.5°	at 768 mm.	(3)		D_4^{20} = 1.0277 (13)	
101.4–102°		(4)		1.0205 (3)	
101.1–101.5°		(5)			n_D^{20} = 1.4130 (11)
101–101.5°	at 730 mm.	(6) (7)			1.4126 (3)
101–102.5°		(8)			1.41209 (13)
100–101.5°		(9)			1.4117 (6) (7)
100–101°		(10)			
100.5°	at 733 mm.	(11)			

Comml. $\bar{C}$ may contain unsatd. and P cpds. (14).

[For prepn. of $\bar{C}$ from *n*-butyric acid (1:1035) with PCl_5 (83% yield (15)), with PCl_3 (yield 69–77% (16)) (9) (17) or PCl_3 + $ZnCl_2$ (77% yield (15)), with $SOCl_2$ (yield: 97.4% (18), 90% (19), 85% (10), 80% (6) (7), 50% (15)) (20), with benzoyl chloride (80–87%

yield (8) (21), with phthalyl dichloride (3:6900) (91.5% yield (22)), with benzotrichloride (3:6540) + $ZnCl_2$ at 70–80° (23), or with $SiCl_4$ in xylene (49% yield (24)) see indic. refs.; *for prepn. of C̄ from α-chloroethyl n-butyrate on warming with a trace of $ZnCl_2$ see (25); for prepn. of C̄ from n-butyric acid (1:1035) by use of methyl chlorosulfonate, benzene*sulfonyl chloride, etc., see (26).]

[C̄ on htg. with n-butyric acid (9) or with sodium n-butyrate yields n-butyric anhydride (1:1126), b.p. 198.2° at 760 mm. (12), f.p. −75.0° (12), D_4^{21} = 0.9687 (27), $n_D^{19.73}$ = 1.4121 (27), n_D^{18} = 1.4143 (28).]

C̄ with Cl_2 in CCl_4 gives (17) a mixt. of α-, β- and γ-chloro-n-butyryl chlorides, some α-chloro-n-butyric acid anhydride also being formed (29); C̄ with SO_2Cl_2 in pres. of dibenzoyl peroxide gives (30) 15% α-chloro-n-butyryl chloride (3.5570), 55% β-chloro-n-butyryl chloride (3.9100), and 30% γ-chloro-n-butyryl chloride (3.5970). — For study of mech. of chlorination see (31). — [For action of PCl_5 on C̄ see (32).]

[C̄ with Br_2 in light yields (17) (33) (14) (34) α-bromo-n-butyryl chloride, b.p. 151–153° (34), and β-bromo-n-butyryl chloride.]

[*C̄ on cat. hydrogenation with H_2 + Pd-$BaSO_4$ cat. in ether (35) or in vapor phase (36)* gives n-butyraldehyde (1:0130), b.p. 74.7°; C̄ on reduction with Na/Hg or Na in moist ether yields (37) (38) (39) *octene-4-diol-4,5 di-n-butyrate*.]

[C̄ added to large excess of certain RMgX cpds. in ether is in part reduced and in part undergoes normal formn. of corresp. ketone: e.g., C̄ with *ter*-BuMgCl gives 9% reduction and 71% ketone formn. (6) (7) (11), products include n-butyl n-butyrate, *ter*-butyl n-propyl ketone (2,2-dimethylhexanone-3), and *ter*-butyl-n-propyl-carbinyl n-butyrate. — C̄ with excess C_6H_5MgBr gives (84% yield (40)) 1,1-diphenylbutene-1 [Beil. V-648, V_1-(313)].]

[C̄ with chlorosulfonic acid at room temp. (41) or with $AlCl_3$ in $CHCl_3$ followed by aq. (42) gives di-n-propyl ketone (butyrone) (1.5447), b.p. 144°. — Note, however, that C̄ on htg. with $AlCl_3$ at 60° without $CHCl_3$, then poured into aq., yields (42) (43) 2,4,6-triethylphloroglucinol [Beil. VI-1129], m.p. 107°.]

[C̄ with ethylene + $AlCl_3$ at 20° gives (70% yield (44)) (45) β-chloroethyl n-propyl ketone (1-chlorohexanone-3) [Beil. I-690]; C̄ with cyclohexene + $SnCl_4$ yields (46) 1-cyclohexenyl n-propyl ketone, b.p. 100–102° at 8 mm., D_4^{14} = 0.950, n_D^{14} = 1.4885 (oxime, m.p. 67°, semicarbazone, m.p. 175°) (46); C̄ with cyclohexane + $AlCl_3$ yields (47) α-methyl-cyclopentyl n-propyl ketone.]

[C̄ with C_6H_6 + $AlCl_3$ gives (89% yield (48)) (16) phenyl n-propyl ketone (butyrophenone) (1:5535), b.p. 230°; *C̄ with toluene + $AlCl_3$ gives (49) n-propyl p-tolyl ketone* Beil. VII-330, VII_1-(175)], b.p. 250°.]

[C̄ with $AlCl_3$ + *phenol yields (50) (51) (20)* 45% o-(n-butyryl)phenol, b.p. 124–126° at 14 mm. (51), 119° at 9 mm. (50), m.p. 10.5–10.6° (50), 8° (51), D_{25}^{25} = 1.0683 (50), $n_D^{25.5}$ = 1.5375 (50) (semicarbazone, m.p. 192–193° (50), phenylhydrazone, m.p. 85–87° (51)), and 30% p-(n-butyryl)phenol, b.p. 200° at 15 mm. (51), 187–189° at 9 mm. (50), m.p. 91–91.5° (50) (benzoate, m.p. 107–107.5° (50), 106–107° (51)); for reactn. of C̄ with carvacrol (1:1760) + $AlCl_3$ in nitrobenzene see (52), similarly with thymol (1:1430) see (53).]

C̄ on hydrolysis yields n-butyric acid (1:1035), b.p. 164°; for the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see n-butyric acid (1:1035).

3:7370 (1) Timmermans, *Bull. soc. chim. Belg* **36**, 507 (1927). (2) Koehl, Wenzke, *J. Am. Chem. Soc.* **59**, 1418 (1937). (3) Martin, Partington, *J. Chem Soc.* **1936**, 162. (4) Reitter, *Z physik. Chem* **36**, 137 (1901). (5) Kohlrausch, Pongratz, *Z. physik Chem.* **B-22**, 381 (1933). (6) Greenwood, Whitmore, Crooks, *J. Am Chem. Soc* **60**, 2028–2030 (1938). (7) Whitmore, *Rec. trav chim.* **57**, 565 (1938). (8) Brown, *J. Am Chem Soc* **60**, 1325–1328 (1938). (9)

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C̄ gives n
3:7155).]
C̄ on oxid

:7390 (1) F
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—— *dl*-(α,γ-Dimethylallyl) *p*-nitrobenzoate: m.p. 56° (11). [? of corresp. alcohol (11).]

—— *dl*-(α,γ-Dimethylallyl) *N*-(α-naphthyl)carbamate: m.p. ... details regarding this see (11).]

3:7400 (1) Bötteher (to I.G.), Ger. 512,232, Nov. 7, 1930; Cent. 1931, I (1931). (2) Beil, *Ber.* 41, 2741 (1908). (3) Bradenahm, Bull. ... (1929); *Cent.* 1929, I 2966; *C.A.* 23, 4196 (1929). (4) Arm. Seeb. J. C 1749 (5) Shoale, Wallis, *J. Am. Chem. Soc.* 53, 4250 (1931). (6) *Chem.* 81, 705 (1929). (7) Hills, Kenyon, Phillips, *J. Chem. Soc.* 1936; *J. Am. Chem. Soc.* 53, 1920 (1931). (9) Bötteher (to I.G.), Ger. ... *Cent.* 1929, I 3017; *C.A.* 23, 2022 (1929). (10) Hesse, Chem. ... 3174–3176 (1941).
(11) Balfe, Hills, Kenyon, Phillips, Platt, *J. Chem. Soc.* 1942, 55–62.

3:7405 ISOPROPYL CHLOROFORMATE $C_4H_7O_2Cl$

(Isopropyl chlorocarbonate) $(CH_3)_2CH.O.CO.Cl$

B.P. 103–104° (1) (2) at 723 mm. (3)

Colorless liq. insol. cold aq.

[For prepn. (40% yield (2)) from isopropyl alc. (1:6135) + phosgene (3); using diphosgene (3:5515) see (1).]

C̄ on htg. with quinoline dec. at 62° (4) into isopropyl chloride ... higher temp. some propylene is also formed: for study see (5).]

Ⓓ **Isopropyl carbamate** [Beil. III-29]: from C̄ in C_6H_6 by treatment ... filtration of pptd. NH_4Cl, and evapn. of solvent; long ndls., m.p. 92– ...

Ⓓ **Isopropyl *N*-phenylcarbamate** (isopropyl carbanilate) [Beil. XII- ... aniline; cryst. from pet. ether, m.p. 75–76° (6). [Previous ... ous.]

3:7405 (1) Nekrassow, Melnikow, *J. prakt. Chem.* (2) 127, 215 (1930). (2) *J. Am. Chem. Soc.* 47, 436–437 (1925). (3) Thiele, Dent, *Ann.* 302, 269–270 (1 ... *Bull. soc. chim.* (5) 3, 1072 (1936). (5) Compere, *Proc. Louisiana Acad. Sci.* ... *C.A.* 36, 2770 (1942). (6) Weizmann, Garrard, *J. Chem. Soc.* 117, 328 (1920)

3:7410 5-CHLOROPENTENE-1 C_5H_9Cl

$\overset{\displaystyle Cl}{\underset{|}{}}$
$CH_2.CH_2.CH_2.CH{=}CH_2$

B.P.		
103.5–104.5°	at 773 mm. (1)	$D_4^{20} = 0.9125$ (1) $n_D^{20} =$
105°	at 745 mm. (2)	$D_{15}^{19} = 0.916$ (2) $n_D^{19} = 1$
30.5°	at 61 mm. (1)	

Colorless limpid liq. with odor like allyl chloride but weaker; alm. insol. aq.

[For prepn. of C̄ from penten-1-ol-5 with PCl_3 + pyridine (1) or with $SOCl_2$ + aniline (2) see indic. refs.]

[For study of rate of reactn. of C̄ with KI in acetone see (1).]

—— **5-Phthalimidopentene-1**: m.p. 40°, b.p. 155–157° at 12 mm. (3). [Not from C̄ but obtd. in 90% yield (3) from 5-bromopentene-1 with K phthalimide in xylene at 150–160° for 6 hrs.]

3:7410 (1) Juvala, *Ber.* 63, 1991–1997 (1930). (2) Paul, *Compt. rend.* 193, 598 (1931). (3) Kharasch, Fuchs, *J. Org. Chem.* 9, 370 (1944).

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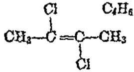
3:7395 *trans*-**2,3-DICHLOROBUTENE-2** $C_4H_6Cl_2$ **Beil. S.N. 11**



B.P. 101–103° at 758 mm. (*1*) $D_4^{20} = 1.1416$ (*1*) $n_C^{19} = 1.4539$ (*1*)

$D_4^{18} = 1.1421$ (*1*)

[*See also cis stereoisomer* (3:5500).]

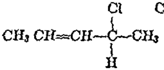
[For prepn. of $\bar{C}$ (accompanied by its *cis* stereoisomer (3:5500)) from 2,2,3-trichlorobutane (3:5680) with solid KOH (*1 mole*) at 135–140° see (*1*).]

$\bar{C}$ on oxidn. with 3% aq. KMnO [illegible] (1:1010).

$\bar{C}$ in CCl_4 at −20° tr [illegible], yields (*1*) acetic acid (1:1010) + acetaldehyde (1:0100).

3:7395 (*1*) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1553–1558 (1936); *Cent.* **1937**, I 3785; *C.A.* **31**, 2165 (1937).

3:7400 *d,l*-**4-CHLOROPENTENE-2** C_5H_9Cl **Beil. I - 210**
(2-Chloropentene-3; I_1—
α,γ-dimethylallyl chloride, I_2-(185)
α-methylcrotyl chloride,
piperylene hydrochloride)



B.P.			
103° dec.	at 760	mm.	(*1*)
103–106°			(*2*)
100.5°	at 771.6	mm.	(*3*)
68°	at 270	mm.	(*4*)
65°	at 200	mm.	(*3*)
57°	at 200	mm.	(*10*)
58°	at 166	mm.	(*5*)
18–20°	at 12–13	mm.	(*1*)

$D_4^{20} = 0.9004$ (*3*) (*10*)

$n_D^{25} = 1.4311$ (*5*)

$n_D^{20} = 1.4322$ (*3*)
1.4328 (*10*)

Two geom. stereoisomers of $\bar{C}$ are possible but as yet unrecognized. — [A levorotatory form of $\bar{C}$ has been obtd. (*6*) (*7*) cf. (*11*). — $\bar{C}$ *does not* undergo allylic transposition.]

[For prepn. of $\bar{C}$ from penten-2-ol-4 with HCl gas in the cold (*3*) (*5*), with PCl_3 in dry ether (37% *yield* (*8*)) or with pyridine (*4*), with PCl_5 (*2*) see indic. refs.]

$\bar{C}$ is readily hydrolyzed even by cold aq. (*3*); with KOH gives Sap. Eq. 106.2 (calcd. 104.6) (*4*). [For study of mech. of hydrolysis of $\bar{C}$ see (*4*).]

[$\bar{C}$ with HBr gives (*3*) 4-bromopentene-2; with phenol as specified (*8*) gives phenyl *α,γ*-dimethylallyl ether, with diethyl sodiomalonate gives the substituted ester (*5*); for reactn. of $\bar{C}$ with various aliphatic and aromatic amines see (*9*).]

[$\bar{C}$ with *n*-propyl MgCl yields (*10*) 4-methylheptene-2, b.p. 113.5° at 760 mm., $D_4^{20} = 0.7206$, $n_D^{20} = 1.4123$ (*10*).]

—— *d*-(*α,γ*-**Dimethylallyl**) **acetate**: b.p. 136–137° (*11*). [From the corresp. *d*-alcohol with Ac_2O + pyridine (*11*).]

—— *d,l*-(*α,γ*-**Dimethylallyl**) **benzoate**: b.p. 140° at 21 mm.; $n_D^{22} = 1.5075$ (*11*). [From the corresp. *d*-alcohol with BzCl + pyridine (*11*).]

—— *d,l*-(α,γ-Dimethylallyl) *p*-nitrobenzoate: m.p. 56° (11). [From the *d*- or *d,l*-forms of corresp. alcohol (11).]

—— *d,l*-(α,γ-Dimethylallyl) *N*-(α-naphthyl)carbamate: m.p. 105° (11). [For important details regarding this see (11).]

3:7400 (1) Böttcher (to I.G.), Ger. 512,232, Nov. 7, 1930; *Cent.* **1931**, I 1007; *C.A.* **25**, 1037 (1931). (2) Reif, *Ber.* **41**, 2711 (190
(1929); *Cent.* **1929**, I 2966; *C.A.* **23**,
1749. (5) Shonle, Waldo, *J. Am.*
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Cent. **1929**, I 3037; *C.A.* **23**, 3052 (1929). (10) Henne, Chanan, Turk, *J. Am. Chem. Soc.* **63**, 3474–3476 (1941).
(11) Balfe, Hills, Kenyon, Phillips, Platt, *J. Chem. Soc.* **1943**, 348–351.

3:7405 ISOPROPYL CHLOROFORMATE $C_4H_7O_2Cl$ Beil. III - 12

(Isopropyl chlorocarbonate) $(CH_3)_2CH.O.CO.Cl$ III_1—

III_2-(10)

B.P. 103–104° (1) (2) at 723 mm. (3)

Colorless liq. insol. cold aq.

[For prepn. (40% yield (2)) from isopropyl alc. (1:6135) + phosgene (3:5000) see (2) (3); using diphosgene (3:5515) see (1).]

C̄ on htg. with quinoline dec. at 62° (4) into isopropyl chloride (3:7025) + CO_2. [At higher temp. some propylene is also formed: for study see (5).]

Ⓓ Isopropyl carbamate [Beil. III-29]: from C̄ in C_6H_6 by treatment with NH_3 gas, filtration of pptd. NH_4Cl, and evapn. of solvent; long ndls., m.p. 92–93° (3).

Ⓓ Isopropyl *N*-phenylcarbamate (isopropyl carbanilate) [Beil. XII-321]: from C̄ + aniline; cryst. from pet. ether, m.p. 75–76° (6). [Previous recorded values are erroneous.]

3:7405 (1) Nekrassow, Melnikow, *J. prakt. Chem.* (2) **127**, 215 (1930). (2) Hamilton, Sly, *J. Am. Chem. Soc.* **47**, 436–437 (1925). (3) Thiele, Dent, *Ann.* **302**, 269–270 (1898). (4) Carré, *Bull. soc. chim.* (5) **3**, 1072 (1936). (5) Compere, *Proc. Louisiana Acad. Sci.* **6**, 93–98 (1942); *C.A.* **36**, 2779 (1942). (6) Weizmann, Garrard, *J. Chem. Soc.* **117**, 328 (1920).

3:7410 5-CHLOROPENTENE-1 C_5H_9Cl Beil. S.N. 11

Cl
|
$CH_2.CH_2.CH_2.CH{=}CH_2$

B.P.

103.5–104.5° at 773 mm. (1)	D_4^{20} = **0.9125** (1)	n_D^{20} = **1.42973** (1)
105° at 745 mm. (2)		
36.5° at 61 mm. (1)	D_{15}^{19} = **0.916** (2)	n_D^{19} = **1.43055** (2)

Colorless limpid liq. with odor like allyl chloride but weaker; alm. insol. aq. (1).

[For prepn. of C̄ from penten-1-ol-5 with PCl_3 + pyridine (1) or with $SOCl_2$ + dimethylaniline (2) see indic. refs.]

[For study of rate of reactn. of C̄ with KI in acetone see (1).]

—— **5-Phthalimidopentene-1:** m.p. 40°, b.p. 155–157° at 12 mm. (3). [Not reported from C̄ but obtd. in 90% yield (3) from 5-bromopentene-1 with K phthalimide in xylene at 150–160° for 6 hrs.]

3:7410 (1) Juvala, *Ber.* **63**, 1994–1997 (1930). (2) Paul, *Compt. rend.* **193**, 599 (1931). (3) Kharasch, Fuchs, *J. Org. Chem.* **9**, 370 (1944).

3:7415 2,2-DICHLOROBUTANE $C_4H_8Cl_2$ Beil. I - 119, I_1—, I_2—

$$CH_3.CH_2.\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}.CH_3$$

B.P.		M.P.		
104–104.5°	(1)	**−74°** (3)	D_4^{20} = **1.0665** (2)	n_D^{20} = **1.4306** (2)
102–104°	(2) (3)			
99–102° at 760 mm.	(4) (5)		$D_4^{21.8}$ = **1.069** (5)	n_D^{22} = **1.4270** (4)

[For prepn. from butanone (ethyl methyl ketone) (1:5405) with PCl_5 see (8) (5) (4) (6) (1); for formn. (together with other isomers and 2-chlorobutene-1 (1)) from 2-chlorobutane (3:7125) by chlorination see (2).]

$\bar{C}$ with alc. KOH splits off HCl and gives mixt. of both stereoisomeric 2-chlorobutene-2's (2) (9) (3:7105). [Cleavage of HCl in the other sense to yield mainly 2-chlorobutene-1 (3:7075) is also claimed (7).]

3:7415 [illegible] *Ber.* 8, 412 (1875). (7) Schjanberg, *Ber.* **71**, 573 (1938). (8) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* **61**, 940 (1939). (9) Charpentier, *Bull. soc. chim.* (5) **1**, 1407–1411 (1934).

3:7420 1-CHLOROPENTENE-1 C_5H_9Cl Beil. S.N. 11

$$CH_3.CH_2.CH_2.CH{=}\overset{\displaystyle Cl}{C}H$$

B.P. 102–106° (1)

Two geom. stereoisomers of $\bar{C}$ are possible but as yet unrecognized.

[For prepn. of $\bar{C}$ from 1,2-dichloropentane (3:8140) with alc. KOH see (1).]

3:7420 (1) Lemke, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1995–1998 (1937); *Cent.* **1939**, I 2398; *C.A.* **32**, 482 (1938).

3:7425 1,1-DICHLORO-2-METHYLPROPANE $C_4H_8Cl_2$ Beil. I - 126, I_1—, I_2—

(Isobutylidene (di)chloride)

$$CH_3.\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}.CHCl_2$$

B.P.		
105–106°	(1)	D_{12}^{12} = **1.0111** (5)
104.3–105.7°	(2)	
108°	(3)	
103–105°	(5)	

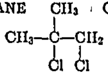
Colorless liq. with agreeable odor.

[For prepn. from isobutyraldehyde (1:0120) + PCl_5 see (5) (2); for formn. (with other products) during chlorination of isobutane see (1) (3).]

$\bar{C}$ htd. in s.t. with $Ag_2O + H_2O$ yields Ag isobutyrate (4).

3:7425 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* **27**, 1191 (1935). (2) Kohlrausch, Köppl, *Monatsh.* **65**, 197 (1935). (3) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,072, June 4, 1935; *Cent.* **1936**, I 3012. (4) Spring, Lecrenier, *Bull. soc. chim.* (2) **48**, 626 (1887). (5) Oeconomides, *Bull. soc. chim.* (2) **45**, 497–498 (1881).

3:7430 1,2-DICHLORO-2-METHYLPROPANE (Isobutylene dichloride) $C_4H_8Cl_2$ Beil. I - 120, I_1-(41), I_2-(88)



B.P.			
106.5° cor. at 760 mm. (1)	D_4^{20} = 1.080 (4)	n_D^{20} = 1.4370 (1)
107–108° (3) (4) (5) (6) (7)		1.4360 (4)
59–60° at 150 mm. (1)	D_{20}^{20} = 1.093 (1)	n_D^{17} = 1.4373 (3)
38.6–39.2° at 70 mm. (1)		

Liq. with mild clean sweetish odor; stable on stdg. and develops no HCl even in 6 months (1).

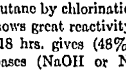
[For prepn. from *ter*-butyl chloride (3:7015) by chlorination see (1) (2) (8); from 2-methylpropene (isobutylene) by addn. of Cl_2 at 0° see (4); from 1-chloro-2-methylpropanol-2 (3:7752) with conc. HCl see (2) (9); from isobutane by chlorination see (10).]

Upon hydrolysis the tertiary chlorine atom shows great reactivity, the primary chlorine atom little. Thus $\bar{C}$ on boiling with aq. for 18 hrs. gives (48% yield (2)) 1-chloro-2-methylpropanol-2 (3:7752). [The addn. of bases (NaOH or $NaHCO_3$) or antiacids ($CaCO_3$) results in lower yields (2).] [In addn. to the above 1-chloro-2-methylpropanol-2 the presence of $NaHCO_3$ or Na_2CO_3 leads (11) to formn. of 2-methylpropanediol-1,2 (isobutylene glycol) [Beil. I-480], 1-chloro-2-methylpropene-1 ("isocrotyl chloride") (3:7120), and isobutyraldehyde (1:0120).] [For study of methods of conversion of $\bar{C}$ to isobutyraldehyde see (1).]

3:7430 (1) Hersh, Nelson, ... ks, Nelson, *J. Am. Chem. Soc.* 58, 1010–1011 ... . B-48, 10 (1941). (4) Burgin, Engs, Groll, I... s, McBee, Weber, *Ind. Eng. Chem.* 27, 110... -534 (1900). (7) Pogorshelski, *J. Russ. Ph*... 668. (8) Rogers, Nelson, *J. Am. Chem. Sc*... . 142, 496 (1900). (10) Hass, McBee (to Pu... 1935; *Cent.* 1936, I 3012.

(11) Dobryanskii, Gutner, Shchigel'skaya, *J. Gen. Chem.* (*U.S.S.R.*) 7, 1315–1320 (1937); *Cent.* 1938, I 561; *C.A.* 31, 6189 (1937).

3:7450 α,α-DIMETHYLPROPIONYL CHLORIDE (Trimethylacetyl chloride; pivalyl chloride) C_5H_9OCl Beil. II - 320, II_1-(139), II_2-(280)



B.P.		B.P.		
107°	(1)	70.5°–71.0° at 250 mm. (5) (6)		n_D^{20} = 1.4126 (7)
105–106°	(2)	58° at 150 mm. (7)		1.4125 (9)
104.3–105.4°	(3)	57.6° at 150 mm. (8)		1.4123 (9)
103–104°	(4)	56° at 150 mm. (9)		1.4122 (8)
		48° at 100 mm. (9)		1.4118 (5) (6)

[For prepn. of $\bar{C}$ from trimethylacetic acid (pivalic acid) (1:0410) with PCl_5 (2), with PCl_3 (10), with $SOCl_2$ (11) (yield 80% (5) (6) (8), 86% (7)), or with benzoyl chloride (1 mole 70% yield, 2 moles 92% yield (4) cf. (16)) see indic. refs.; for formn. of $\bar{C}$ (together with other prods.) from isobutane + CO + $AlCl_3$ at 20° and 120 atm. see (12).]

[$\bar{C}$ with MeOH gives (50% yield (8)) methyl trimethylacetate (1:3072), b.p. 99.5° at

731 mm., n_D^{20} = 1.3895 (8); C̄ with sodium trimethylacetate yields (2) pivalic anhydride, b.p. 124° at 93 mm., n_D^{20} = 1.4093 (6).]

[C̄ with large excess of most Grignard reagents is reduced to *ter*-butyl carbinol (neopentyl alcohol) (1:5812), other products also being formed; for reactn. of C̄ with EtMgBr (8) (13), with *n*-PrMgBr (13), with *iso*-PrMgBr (13), with *n*-BuMgBr (5) (7) (13), with *iso*-BuMgBr (13) or *iso*-BuMgI (9), with *ter*-BuMgCl (5) (6) (9), with *n*-AmMgBr (13), with *iso*-AmMgBr (13), with *ter*-AmMgCl (9), with neopentyl MgCl (9) see indic. refs.]

[For study of rate of reactn. of C̄ with various alcs. see (14).]

C̄ on hydrolysis yields trimethylacetic acid (1:0410) q.v. (for the amide, m.p. 132.0–132.6° cor. (15), anilide, m.p. 132° cor. (16), *p*-toluidide, m.p. 119.5° cor. (16), and other derivatives (16) corresp. to C̄ see 1:0410 and indic. refs.).

3:7450 (1) Böeseken, *Rec. trav. chim.* **29**, 99 (1910). (2) Butlerow, *Ann.* **173**, 373–374 (1874). (3) Kohlrausch, Pongratz, *Z. physik. Chem.* **B-22**, 382 (1933). (4) Brown, *J. Am. Chem. Soc.* **60**, 1325–1328 (1938). (5) Whitmore, *Rec. trav. chim.* **57**, 562–568 (1938). (6) Greenwood, Whitmore, Crooks, *J. Am. Chem. Soc.* **60**, 2028–2030 (1938). (7) Whitmore, Popkin, Whitaker, Mattil, Zech, *J. Am. Chem. Soc.* **60**, 2458–2462 (1938). (8) Whitmore, Foster, *J. Am. Chem. Soc.* **64**, 2966–2968 (1942). (9) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* **63**, 643–654 (1941). (10) Whit[illegible] *J. Am. Chem. Soc.* **51**, [illegible] [illegible] iari, *Ber.* **69**, [illegible] –2789 (1938). [illegible] n. *Chem. Soc.* **67**, 1785 (1945). (16) Degnan, Shoemaker, *J. Am. Chem. Soc.* **68**, 105 (1946).

3:7455 5-CHLOROPENTENE-2 C_5H_9Cl Beil. S.N. 11

(1-Chloropentene-3) $CH_3.CH{=}CH.CH_2CH_2Cl$

B.P.

107.0–107.6° at 755 mm. (1) **D_4^{20} = 0.9043 (1)** **n_D^{20} = 1.4310 (1)**

Two geom. stereoisomers of C̄ are possible but as yet unrecognized.

[For prepn. of C̄ in 75% yield from penten-3-ol-1 with $SOCl_2$ in CH_2Cl_2 see (1).]

C̄ with NaI in acetone gives (1) after 11 hrs. reflux 74% yield 1-iodopentene-3, b.p. 53.6° at 20 mm., D_{14}^{20} = 1.5579, n_D^{20} = 1.5153 (1).

C̄ with Mg in dry ether yields RMgCl (used in reactn. with acrolein (1:0115) to give (50% yield (1)) penten-3-yl-vinyl-carbinol).

3:7455 (1) Goethals, *Bull. soc. chim. Belg.* **46**, 417–419 (1937).

3:7460 1-CHLOROPENTANE $C_5H_{11}Cl$ Beil. I - 130

(*n*-Amyl chloride, $CH_3.CH_2.CH_2.CH_2.CH_2Cl$ I_1-(42)

n-butylcarbinyl chloride) I_2-(95)

B.P.			F.P.	
108.35° cor.	**at 760 mm.**	**(1) (2)**	**−99° (2)**	**D_4^{25} = 0.87667 (2)**
107.74–107.78°	**at 760 mm.**	**(3)**		**n_D^{25} = 1.41026 (2)**
107–108°		**(4)**		**D_4^{20} = 0.8828 (8)**
105.7–105.8°	**at 759.3 mm.**	**(5)**		**0.8821 (30)**
105°	**at 764 mm.**	**(30)**		**0.8816 (2)**
107.8–108.4°	**at 749.7 mm.**	**(6)**		**n_D^{20} = 1.41280 (8)**
106.6°	**at 739.8 mm.**	**(7)**		**1.41253 (2)**
106°	**at 725 mm.**	**(8)**		**1.41177 (30)**
				D_4^{15} = 0.88657 (2)
				n_D^{15} = 1.41481 (2)

Note that most samples of C̄ reported prior to 1938 undoubtedly contained a small amount of mixed 2-chloropentane (3:7325) and 3-chloropentane (3:7330). This previously unrecognized fact may be the cause of much variation in reported physical constants, especially the refractive index.

[For prepn. of C̄ (or its mixt. with 2-chloro- and 3-choropentane) from pentanol-1 (1:6205) with conc. HCl (7) (4) in s.t. at 120° for 12–15 hrs. (94% yield (2)) see indic. refs.; with HCl + $ZnCl_2$ (yield: 67% (30), 57% (8), 72% (9)) see (8) (9) (30); with PCl_3 + $ZnCl_2$ (70% yield (9)) or PCl_5 + $ZnCl_2$ (76% yield (9)) see (9); with $SOCl_2$ + pyridine (gives no rearrangement (8)) (yield: 80% (8), 87% (9)) see (8) (9); for prepn. (23% yield (10)) from γ-chloropropyl *p*-toluenesulfonate by reactn. with EtMgBr see (10).]

[For formn. of C̄ (together with other products) during chlorination of pentane see (11) (12) (13) (14).]

C̄ with EtOH forms const.-boilg. mixt., b.p. 72.5°, but forms no azeotrope with MeOH. C̄ forms with aq. a const.-boilg. mixt., b.p. 82°.

C̄ on htg. with conc. HCl + $ZnCl_2$ at 126–134° for 12 hrs. undergoes partial isomerization forming 3% of a mixt. of 2-chloropentane (3:7325) and 3-chloropentane (3:7330) (8).

[For study of rate of hydrolysis by aq. at 80° and 180°, and rate of cleavage of HCl at 180°, see (11); for rate of reactn. with KI in acetone see (4) (15) (16); for reactn. with Na—C≡CH see (17) (18); with KCN see (19); with Cl_2 see (6); for extensive study of reactn. with Na see (19) (20) (21) (22) (23) (24) (25).]

Ⓓ ***n*-Caproanilide:** C̄ with Mg in dry ether yields RMgCl which upon reactn. with phenyl isocyanate and subsequent hydrolysis yields (26) *n*-caproanilide, m.p. 96° cor. (27), 94–95° u.c. (26), 92° (28).

Ⓓ ***n*-Capro-*p*-toluidide:** m.p. 74–75° u.c. (26), 73° (28). [From RMgCl + *p*-tolyl isocyanate as above (26).]

Ⓓ ***S*-*n*-Amylisothiourea picrate:** m.p. 154° (29). [From C̄ in alc. on refluxing 2 hrs. with thiourea, followed by addn. of PkOH (29).]

—— ***N*-(*n*-Amyl)tetrachlorophthalimide:** ndls. from $CHCl_3$, poured into 2 vols. MeOH, m.p. 145–146° (31).

3:7460 (1) Hass, *J. Chem. Education* **13**, 492–493 (1936). (2) Simon, *Bull. soc. chim Belg.* **38**, 48, 56, 58 (1929). (3) Rintelen, Saylor, Gross, *J. Am. Chem. Soc.* **59**, 1129 (1937). (4) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 245 (1924). (5) Karvonen, *Ann. Acad. Sci. Fennicae* **3-A**, 1–103; *Cent.* **1912**, II 1271. (6) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941). (7) Lieben, Rossi, *Ann.* **159**, 72 (1871). (8) Whitmore, Karnatz, Popkin, *J. Am. Chem. Soc.* **60**, 2540–2542 (1938). (9) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (10) Rossander, Marvel, *J. Am. Chem. Soc.* **50**, 1495 (1928).

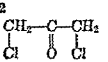
(11) Ayres, *Ind. Eng. Chem.* **21**, 899–904 (1929). (12) Clark, *Ind. Eng. Chem.* **22**, 439–443 (1930). (13) Ayres (to B.A.S. Co.), U.S. 1,741,393, Dec. 31, 1929; *Cent.* **1930**, I 3353. (14) Sharples Solv. Corp., Ger. 610,660, March 18, 1935; *Cent* **1935**, II 920. (15) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (16) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* **47**, 587–589 (1925). (17) Hurd, Christ, *J. Org. Chem.* **1**, 143–144 (1936). (18) Vaughn, Hennion, Vogt, Nieuwland, *J. Org. Chem.* **2**, 1–22 (1937). (19) Hass, Marshall, *Ind. Eng. Chem.* **23**, 352–353 (1931). (20) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 757 (1936).

(21) Morton, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 1700 (1936). (22) Morton, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 2599–2605 (1936). (23) Morton, Richardson, *J. Am. Chem. Soc.* **62**, 123–126 (1940). (24) Morton, Richardson, *J. Am. Chem. Soc.* **62**, 129–131 (1940). (25) Gilman, Pacevitz, *J. Am. Chem. Soc.* **62**, 1301–1302 (1940). (26) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2119 (1934). (27) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1065 (1931). (28) Robertson, *J. Chem. Soc.* **115**, 1220–1221 (1919). (29) Levy, Campbell, *J. Chem. Soc.* **1939**, 1443. (30) Vogel, *J. Chem. Soc.* **1943**, 638, 640.

(31) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934).

3:0563 1,3-DICHLOROPROPANONE-2 $C_3H_4OCl_2$ Beil. I - 655
I_1-(344)
I_2-(719)

(α,α'-Dichloroacetone,
sym.-dichloroacetone,
bis-(chloromethyl) ketone)



M.P.		B.P.			
45°	(1) (2)	173.0–173.4° cor. at 759 mm.	(4)	D_4^{46} = 1.3843	(4)
44°	(16)	172.6–173.0° cor. at 748 mm.	(4)	1.3809	(4)
43–44°	(3) (8)	172.3–172.8° cor.	(1)		
43°	(4) (19)	172–173°	(3)	n_D^{46} = 1.47223	(4)
42.5–43°	(7)	172°	(2) (9) (20)	1.47144	(4)
42.5°	(5) (20)	170–171°	(6)		
42–43°	(4) (22)	170°	(8)		
		168–169° at 723 mm.	(7)		

Colorless tbls. or ndls. volatile even at ord. temp. — Vapors are lachrymatory; liquid blisters skin. — Appreciably sol. in aq. especially on warming, eas. sol. alc., ether. — Volatile with steam.

[For prepn. of Č from 1,3-dichloropropanol-2 (glycerol α-dichlorohydrin) (3:5985) by oxidn. with $Na_2Cr_2O_7$ + H_2SO_4 (68–75% yield (10)), with $K_2Cr_2O_7$ + H_2SO_4 (1) (2) (4) (6) (7) (8) (9) (11) (generally poorer yields) see indic. refs (note also that b.p. of Č is very close to that of the precursor 1,3-dichloropropanol-2 (3:5985), a fact which leads to some doubt as to the true yield of Č in certain of the older reports); for prepn. of Č from acetone (1:5400) with Cl_2 directly (12), in pres. of I_2, $FeCl_3$, or $SbCl_5$ (yield: 28% Č accompanied by 48.6% *unsym.*-dichloroacetone (3:5430) (13)), in pres. of $NiCl_2$ at 70° (other prods. are also formed (14)), or in pres of aq. + $CaCO_3$ (yield: 10% Č accompanied by other prods. (16)) (4) (15), see indic refs]

[For prepn. of Č from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5358) with S_2Cl_2 (yield: 33% Č accompanied by 67% *1,3-dichloropropanol-2 (3:5985)* (17)), from ethyl γ-(α)-chloro-α(γ)-ethoxyacetoacetate (18) or from ethyl α,γ-dichloracetoacetate (19) by ketonic cleavage with HCl, from allene (propadiene) (20) or 1,2-dichloropropene-2 (21) with HOCl, or from 1,3-diiodoacetone on digestion with AgCl (22) cf. (3) see indic. refs]

[Č on reduction with yeast gives (53% yield (2)) 1,3-dichloropropanol-2 (3:5985), b.p. 178° (2). — Č with Zn + AcOH does *not* give acetone but yields (23) a gas formerly supposed to have been cyclopropanone (since it yielded with semicarbazide a semicarbazone, m.p. 156° (23)) although in the light of later work (24) (25) (26) this now appears very doubtful. — For polarographic study of reduction potential of Č see (27).]

Č with aq. alk. presumably yields 3-chloropropanone-2-ol-1 [Beil. I-823] and/or propanone-2-diol-1,3 (dihydroxyacetone) [Beil. I-846, I_1-(428), I_2-(889)] since Č readily reduces Fehling's soln. (28).

Č with satd. aq. $NaHSO_3$ soln. yields a $NaHSO_3$ cpd. which seps. with 2½ H_2O (1), 3 H_2O (7). — Č with aq. K_2SO_3 soln. yields (30) corresp. salt of acetone-α,α'-disulfonic acid [Beil. IV_2-(530)].

[Č with KOAc (slightly more than 1 mole) in boilg. AcOH gives (48% yield (29)) chloroacetylmethyl acetate, b p. 112–114° at 16 mm. (29) — Č with K benzoate refluxed in alc. yields (23) 1,3-dibenzoyloxyacetone, long ndls. from alc., but m p. not reported]

[Č in dry MeOH treated with HCl gas gives (81.5% yield (31)) 1,3-dichloroacetone dimethylketal, cryst. from MeOH, m.p. 81.5° (31); Č in abs. EtOH similarly treated gives (smaller yield (31)) 1,3-dichloroacetone diethylketal, m p. 28° (31). — For reactn. of Č with ethylene glycol see (32).]

[For prepn. of C̄ from β,β′-dichlorodiethyl ether (3:6025) with solid NaOH at 200° (1) or with triethanolamine + solid NaOH (70% yield (2)) see indic. refs.]

C̄ is stable toward alkalies but with dil. acids even in cold is readily and quant. hydrolyzed (1) to β-chloroethanol (3:5552) and acetaldehyde (1:0100).

[C̄ with diethyl sodiomalonate gives (73% yield (1)) diethyl β-(vinyloxy)ethyl malonate, b.p. 130–135° at 9 mm., $D_{15}^{15} = 1.0575$ (1); this prod. condenses (1) with urea to give 5-(β-(vinyloxy)ethyl)barbituric acid (whose properties appear to be subsequently unreported) which itself with dil. minl. acid hydrolyzes to give 5-(β-hydroxyethyl)barbituric acid, m.p. above 300° (3). — For analogous reactions of C̄ with various diethyl alkylmalonates and reaction of the products with urea to give the corresp. 5-alkyl-5-(β-(vinyloxy)ethyl)-barbituric acids see (3). — C̄ with diethyl phenyl-sodio-malonate in s.t. at 140–145° for 14 hrs. gives (52% yield (4)) diethyl 5-phenyl-5-(β-(vinyloxy)ethylmalonate, b.p. 196–197° at 17 mm., $D_4^{20} = 1.098$; this prod. with urea gives (4), 5-phenyl-5-(β-(vinyloxy)ethyl)-barbituric acid which upon hydrolysis with dil. acid gives (10% yield (4)) 5-phenyl-5-(β-hydroxyethyl)barbituric acid ("hydroxyluminal").]

[C̄ with phenylacetonitrile gives (50% yield (4)) phenyl-(β-vinyloxyethyl)acetonitrile, b.p. 147° at 8 mm., $D_4^{20} = 1.029$ (4).]

[For use of C̄ in prepn. of cellulose ethers see (5).]

3:7464 (1) ... 1176 (1925). (2) Chitwood, ... 4, 1938; *Cent.* 1938, I 4236; ... 4238; *C.A.* 32, 1278 (1938). ... 925). (4) Nelson, Cretcher, ... Co.), U.S. 2,082,797, June 8,

3:7465 4-CHLORO-2-METHYLBUTENE-2 C_5H_9Cl Beil. I - 214

(γ,γ-Dimethylallyl chloride; isoprene hydrochloride)

Beil. I_1-(88), I_2-(101)

```
Cl          CH3
|           |
CH2—CH═C—CH3
```

B.P. 100° (1) $D_4^{20} = $ **0.9335** (1) $n_D^{20} = $ **1.43975** (4)

30–33° at 40 mm. (4)

Colorless liq. with odor like allyl chloride. — C̄ darkens on stdg. and loses HCl on distn. (1).

[For prepn. of C̄ from 2-methylbutadiene-1,3 (isoprene) (1:8020) by 1,4-addn. of dry HCl gas see (1) (4).]

C̄ on htg. in s.t. with KOAc + AcOH (1) or passed over TiO_2 at 425–450° at reduced press. (3) loses HCl yielding isoprene (1:8020), b.p. 34°.

C̄ reduces alk. $KMnO_4$ (1).

C̄ in conc. HCl satd. with HCl gas gives (94% yield (1)) 2,4-dichloro-2-methylbutane (3:8105), b.p. 145–146° (1) cf. (4).

C̄ in $CHCl_3$ adds 1 Br_2, yields (1) 2,3-dibromo-4-chloro-2-methylbutane, oil decomposing on distn. even under reduced press. (1).

[For behavior of C̄ with $AlCl_3$ see (2).]

3:7465 (1) Aschan, *Ber.* **51**, 1303–1307 (1918). (2) Thomas, Carmody, *J. Am. Chem. Soc.* **55**, 3855 (1933). (3) Müller-Cunradi (to I.G.), Ger. 565,160, Nov. 26, 1932. (4) Soday (to United Gas Improvement Co.), U.S. 2,376,396, May 22, 1945; *C.A.* **39**, 3548 (1945).

3:7463 β-CHLOROETHYL ETHYL ETHER C_4H_9OCl Beil. I - 337
(β-Ethoxyethyl chloride) $CH_2O.CH_2CH_3$ I_1-(170)
| I_2—
CH_2Cl

B.P.			
108–109° (1)	D_4^{20} = 0.9945 (5)	n_D^{20} = 1.412 (5)
107–108° (2)	0.98945 (4)	1.41134 (4)
107–108° (3)	0.98841 (7)	
107.0–107.3° at 751.8 mm. (4) (7)		
105–107° (5)	D_4^{15} = 1.003 (5)	
106° u.c. at 728 mm. (6)		

[For prepn. of Č from β-ethoxyethyl alc. ("Cellosolve") (1:6410) with PCl_3 (7) (8) or with $SOCl_2$ + pyridine (20% yield (10)) (11) in $CHCl_3$ (58.3% yield (9)) see indic. refs.; from ethylene chlorohydrin (3:5552) + ethyl alc. (1:6130) + conc. H_2SO_4 at 145° see (1); from ethylene with ethyl hypochlorite (3:7022) (12) or with mixtures yielding the latter, such as EtOH + Cl_2 (85% yield Č (2)) or alc. *N,N*-dichlorobenzenesulfonamide (5), see indic. refs ; from β-iodoethyl ethyl ether with Cl_2, $SbCl_5$, or ICl see (3).]

Č with NaI in acetone refluxed 15 hrs. gives (10) (11) β-ethoxyethyl iodide, b.p. 151–154° (10) (11).

[Č with KSH in s.t. at 65° for 24 hrs. (1) cf. (13) gives (74% yield (1)) β-ethoxyethyl mercaptan, b.p. 125.5–125.8° u.c., D_{20}^{20} = 0.9479 (1) (corresp. $EtOCH_2CH_2SHgCl$, m.p. 152.0–153.5° dec. (1)) accompanied by (13% yield (1)) of bis-(β-ethoxyethyl) sulfide, b.p. 229° cor., also obtd. (51% yield (1)) from Č + alc. Na_2S.]

[Č with excess $NaOC_6H_5$ in alc. htd. 10 days gives (1) β-phenoxyethyl ethyl ether (β-ethoxyphenetole), b.p. 230°. — Č with disodium salt of hydroquinone (1:1590) gives (14) hydroquinone bis-(β-ethoxyethyl ether), m.p. 34–35°, b.p. 210–212° at 25 mm. (14).]

[Č with diethyl malonate + alc. NaOEt gives (14% yield (1)) cf. (15) diethyl β-ethoxyethylmalonate, b.p. 134–138° at 15 mm. (1), 118–119° at 6 mm. (15); D_4^{20} = 1.0199 (15).]

[Č with aniline refluxed 2 hrs. gives (1) *N*-(β-ethoxyethyl)aniline, b.p. 262–263° cor.]

[For reactn. of Č + $NaNH_2$ with α-picoline, with γ-picoline, and with β-collidine see (16).]

3:7463 (1) Swallen, Boord, *J. Am. Chem. Soc.* **52**, 653–659 (1930) (2) Ernst (to A. Wacker Soc. Elektrochem. Ind.), Ger. 537,696, Nov 5, 1931, *Cent.* **1932**, I 1153, *C A.* **26**, 1297 (1932). (3) Henry, *Bull. soc. chim.* (2) **44**, 459 (1885); *Compt. rend.* **100**, 1007 (1885). (4) Karvonen, *Ann. Acad. Sci. Fennicae* **5-A**, 1–139 (1914), *Cent.* **1919**, III 807, *C A.* **14**, 2176 (1920). (5) Sklyarov, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 2121–2125 (1939); *Cent.* **1940**, II 199–200, *C.A* **34**, 4055 (1940). (6) Mohler, Sorge, *Helv. Chim. Acta* **23**, 1208 (1940). (7) Karvonen, *Ann Acad. Sci. Fennicae* **3-A**, No. 7, 1–103 (1912); *Cent.* **1912**, II 1270. (8) Chalmers, *Can. J. Research* **7**, 464–471 (1932); *Cent.* **1933**, I 1759; *C.A.* **27**, 701 (1933). (9) Hurd, Fowler, *J Am. Chem Soc.* **61**, 251 (1939). (10) Smith, Ungnade, Austin, Prichard, Opie, *J. Org Chem* **4**, 339 (1939).

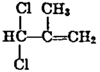
(11) Dutta, *J. Indian Chem. Soc.* **17**, 652 (1940) (12) Suknevich, Chilingaryan, *J. Gen. Chem.* **2**, 783–789 (1932); *Cent.* **1933**, II 1170, *C.A* **27**, 2670 (1933). (13) Rojahn, Lemme, *Arch. Pharm* **263**, 623 (1925). (14) Sexton (to Imperial Chem. Ind., Ltd.), U.S. 2,056,299, Oct. 6, 1936; *Cent.* **1937**, I 1798; *C.A.* **30**, 8641 (1936). (15) Palomaa, Kenetti, *Ber.* **64**, 800–801 (1931). (16) Chichibabine, *Bull. soc. chim.* (5) **5**, 439–441 (1938).

3:7464 β-CHLOROETHYL VINYL ETHER C_4H_7OCl Beil. I —
$CH_2—CH_2—O—CH{=}CH_2$ I_1—
| I_2-(473)
Cl

B.P.
100° cor. at 740 mm. (1) D_{15}^{15} = 1.0525 (1)

3:7475 (1) Whitmore, Bernstein, Mixon, *J. Am. Chem. Soc.* **60**, 2539 (1938). (2) Whitmore, Rothrock, *J. Am. Chem. Soc.* **55**, 1106–1109 (1933). (3) Whitmore, Bernstein, *J. Am. Chem. Soc.* **60**, 2627 (1938).

3:7480 3,3-DICHLORO-2-METHYLPROPENE-1 $C_4H_6Cl_2$ **Beil. S.N. 11**
(1,1-Dichloro-2-methylpropene-2)



B.P.
108–112° at 762 mm. (1) D_4^{24} = **1.1363** (1) n_C^{24} = **1.4523** (1)
49–50° at 120 mm. (1)

Note. C̄ by virtue of allylic transposition may yield derivatives of its synionic isomer 1,3-dichloro-2-methylpropene-1 (3:5590) q.v.

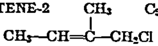
[For prepn. of C̄ (68% yield together with 32% yield of 1,1,2-trichloro-2-methylpropane (3:5710)) from 1-chloro-2-methylpropene-1 (β,β-dimethylvinyl chloride) (3:7120) with Cl_2 (1 mole) + $NaHCO_3$ (1.5 moles) at 0° see (1).]

C̄ on htg. under reflux gives (by allylic transposition) 1,3-dichloro-2-methylpropene-1 (3:5590), b.p. 132°.

C̄ with O_3 followed by hydrolysis yields (1) α,α-dichloroacetone (3:5430) + methylglyoxal (propanone-2-al-1) [Beil. I-762; I_1-(395), I_2-(819)].

3:7480 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939).

3:7485 1-CHLORO-2-METHYLBUTENE-2 C_5H_9Cl **Beil. I —**
(β,γ-Dimethylallyl chloride) I_1—
I_2-(189)



B.P. **110°** at 760 mm. (1) D_4^{20} = **0.9327** (1)
108–110° (2) n_D^{20} = **1.4481** (1)
25.9–26.4° at 25 mm. (1) D_4^{16} = **0.9324** (2)

Note. C̄ by virtue of facile allylic transposition is in equilibrium with its synionic isomer 3-chloro-2-methylbutene-1 (3:7300); reactns. of C̄ therefore may also yield derivatives related to its isomer.

[For prepn. of C̄ (or its mixt. with the synionic 3-chloro-2-methylbutene-1 (3:7300)) by actn. of Cl_2 as specified (1) on "tertiary amylene" (a mixt. consisting mainly of 2-methylbutene-2 (1:8220) with some 2-methylbutene-1 (1:8210)) see (1). — The relative amt. of C̄ and its isomer is not constant but usually is about 40% of C̄ with 60% of 3-chloro-2-methylbutene-1 (3:7300), the ratio, however, being independent of the proportion of the two olefins in the starting material.]

[For formn. of C̄ from 2-methylbutene-2 (1:8220) with Cl_2 see (2); from 2-methylbutene-1 (1:8210) see (3); for prepn. of C̄ (together with other prods.) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhyd. oxalic acid (4) or with Ac_2O + conc. H_2SO_4 (5) see (4) (5); for prepn. of C̄ from 2-methylbuten-2-ol-1 with PCl_3 + pyridine see (1).]

C̄ on hydrolysis gives not only the alc. corresponding to C̄ but also that corresp. to the isomeric 3-chloro-2-methylbutene-1 (3:7300) together with a little ketone: thus C̄ on hydrolysis with 12 pts. aq. at 70° for 16 hrs. gives (6) 25% alc. *A* (2-methylbuten-1-ol-3) [*N*-(α-naphthyl)carbamate, m.p. 91.5–93° (6)] + 50% alc. *B* (2-methylbuten-2-ol-1) [*N*-(α-naphthyl)carbamate, m.p. 103–103.5° (6)] + 5% isopropyl methyl ketone (1:5410);

3:7470 1-CHLOROPENTENE-2 C_5H_9Cl Beil. I —
(γ-Ethylallyl chloride) $CH_3.CH_2.CH{=}CH.CH_2Cl$ I_1—
I_2-(184)

B.P. 109–110°	(1) (2)	D^{23}_{-} = 0.9095 (3)	n_D^{23} = 1.4347 (3)
109.5°	(3)		
106–108°	(4)	$D_4^{21.5}$ = 0.908 (4)	$n_D^{21.5}$ = 1.4352 (4)
62–63.2° at 148 mm.	(5)		

Note. $\bar{C}$ by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer 3-chloropentene-1 (3:7260) q.v.; reactns. of $\bar{C}$ may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of $\bar{C}$ (or its mixt. with 3-chloropentene-1 (3:7260)) from penten-2-ol-1 with dry HCl gas at 0° (5) (7), with PCl_3 + pyridine (4) (7), or with $SOCl_2$ in ether (6) see indic. refs.; for prepn. of $\bar{C}$ from 3-chloropentene-1 (3:7260) by htg. at 225° (60–62% $\bar{C}$) see (6) (3).] [$\bar{C}$ is separable from the accompanying isomer by careful fractional distn. (7) (5).] [For formn. of $\bar{C}$ (together with other products) from pentene-2 (1:8215) + Cl_2 in CCl_4 see (8).]

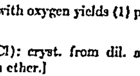
$\bar{C}$ on long shaking with aq. Na_2CO_3 gives (7) in poor yield penten-2-ol-1 (*p*-nitrobenzoate, m.p. 53°) accompanied by much penten-1-ol-3. — $\bar{C}$ on htg. with alc. KOH gives (3) (7) in poor yield the corresp. ethyl ether, viz., 1-ethoxypentene-2, b.p. 123°, D^{23}_{-} = 0.7930, n_D^{23} = 1.4099 (3), accompanied by the isomeric 3-ethoxypentene-1, b.p. 102°, D^{23}_{-} = 0.7768, n_D^{23} = 1.3986 (3).

[For study of reactns. of $\bar{C}$ with KOAc in AcOH, with AgOAc, with *N*-methylaniline, with diethylamine, etc., see (7); for reactn. of $\bar{C}$ with phenol in pres. of K_2CO_3 + acetone see (5).]

Ⓓ *N*-(Penten-2-yl-1)phthalimide [*N*-(γ-ethylallyl)phthalimide]: colorless rhombic cryst. from alc., m.p. 69–70° (7). [From $\bar{C}$ on htg. with K phthalimide in a s.t. at 190–200° for 2½ hrs.; note that some of the corresp. deriv. from the isomer, viz., *N*-(α-ethylallyl)phthalimide, m.p. 78–79°, is formed to extent of about 10% (7).]

3:7470 (1) Mumm, Richter, *Ber.* **73**, 858–860 (1940). (2) Mumm, Hornhardt, Diederichsen, *Ber.* **72**, 107 (1939). (3) Prevost, *Compt. rend.* **187**, 1053–1054 (1928). (4) Gredy, *Bull. soc. chim.* (5) **4**, 419 (1937). (5) Lauer, Filbert, *J. Am. Chem. Soc.* **58**, 1388 (1936). (6) Prevost, *Bull soc. chim.* (4) **49**, 261–267 (1931). (7) Meisenheimer, Link, *Ann.* **479**, 254–277 (1930). (8) Stewart, Weidenbaum, *J. Am. Chem. Soc.* **58**, 98–100 (1936).

3:7475 3-CHLORO-2,2-DIMETHYLBUTANE $C_6H_{13}Cl$ Beil. S.N. 10
(Pinacolyl chloride;
ter-butyl-methyl-carbinyl chloride)



B.P. 109.9° at 734 mm. (1) D_4^{20} = 0.8767 (1) n_D^{20} = 1.4181 (1)

[For formn. of $\bar{C}$ (11%) from 2,2-dimethylbutane (neohexane) (1:8510) on chlorination see (1).] [Note that the corresp. alc. (pinacolyl alc.) (1:6186) with HCl does *not* give $\bar{C}$ but rather rearr. prods. (2).]

$\bar{C}$ with Mg in dry ether gives RMgCl which with oxygen yields (1) pinacolyl alc. (1:6186) q.v.

Ⓓ Pinacolyl mercuric chloride ($C_6H_{13}HgCl$): cryst. from dil. alc., m.p. 89–90° (3); 89.5–90° (2). [From RMgCl + $HgCl_2$ in ether.]

[For density of Č at 0°, 15°, 25°, 50°, and 65°, together with parachors at 0°, 25°, 50°, and 75°, see (9).]

[For prepn. of Č from corresp. alc., dimethyl-n-propyl-carbinol (2-methylpentanol-2) (1:6190) with PCl_5 (6), with HCl gas (1) (2), or with conc. HCl (4) (5) see indic. refs.; for prepn. (68% yield) from ethyl-isopropyl-carbinol (2-methylpentanol-3) (1:6194) with HCl as the result of rearrangement see (1); for formn. (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with HCl + $ZnCl_2$ see (3); for formn. from 2-methylpentene-2 (1:8275) by addn. of HCl see (7) (8).]

[For study of rate of reaction with KI in acetone see (5).]

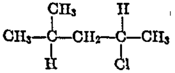
Č with Mg in dry ether yields RMgCl; upon treatment with oxygen this gives (48% yield (1)) of dimethyl-*n*-propyl-carbinol (2-methylpentanol-2) (1:6190) q.v.

- Ⓓ **Dimethyl-*n*-propyl-acetanilide:** m.p. 70.5–74° (3). [From Č via conversion to RMgCl and reaction with phenyl isocyanate (3).]
- Ⓓ **Dimethyl-*n*-propyl-acet-α-naphthalide:** m.p. 116–118° (3). [From Č via conversion to RMgCl and reaction with α-naphthyl isocyanate (3).]

3:7490 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, [illegible] (1938). (2) [illegible], *J. prakt.* [illegible] 1938). [illegible] *Soc.* 47, [illegible] 1937). [illegible] -3111 (1939).

3:7495 ***d,l*-4-CHLORO-2-METHYLPENTANE** $C_6H_{13}Cl$ Beil. I — I_1— I_2-(111)

(*d,l*-Isobutyl-methyl-carbinyl chloride)



B.P. 111–112° at 773 mm. (1) D_4^{20} = **0.861 (1)** n_D^{20} = **1.4113 (1)**

[For prepn. of Č from 2-methylpentanol-4 (1:6199) with dry HCl for 18 weeks (82% yield) see (1); for formn. of Č (together with other products) in reaction of 2-ethylbutanol-1 (1:6223) with HCl + $ZnCl_2$ see (2).]

Č with Mg in dry ether yields RMgCl which with O_2 gives (62% yield (1)) 2-methylpentanol-4 (1:6199) [*N*-(α-naphthyl)carbamate, m.p. 93.5–94.5° (2)]; this alc. upon oxidn. with CrO_3/H_2SO_4 yields (2) 4-methylpentanone-2 (1:5430) q.v.

3:7495 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* 60, 2267 (1938). (2) Whitmore, Karnatz, *J. Am. Chem. Soc.* 60, 2535 (1938).

$\bar{C}$ on hydrolysis with 2 pts. aq. + 1 mole $CaCO_3$ for 4 hrs. at 70° gives (6) 60% alc. *A* + 30% alc. *B* + 5% isopropyl methyl ketone (1:5410); $\bar{C}$ on hydrolysis with CaO for 1½ hrs. gives (6) 70% alc. *A* + 25% alc. *B* + a trace of ketone.

[For study of reactn. of $\bar{C}$ with NaI (4) and its rate of reactn. with KI in acetone at 20° (7) or with NaOEt in alc. at 35° (7) see indic. refs.; the reactivity of the halogenation of *$\bar{C}$ is greater than that in crotyl chloride (1-chlorobutene-2) (3:7205) and the latter in* turn is more reactive than that in methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) or allyl chloride (3:7035), which are about the same (4).]

$\bar{C}$ on treatment with O_3 followed by hydrolysis yields (3) (2) chloroacetone (3:7212) + acetaldehyde (1.0100).

3:7485 (1) Burgin, Engs, Groll, Hearne, *Ind Eng. Chem.* **31**, 1416 (1939). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.) 6, 1116–1132 (1936); Cent. 1937, I 572, C.A. 31, 1003 (1937).* (3)

3:7487 ***ALLYL CHLOROFORMATE*** *$C_4H_5O_2Cl$* ***Beil. III - 12***
(Allyl chlorocarbonate) $Cl.CO.O.CH_2.CH{=}CH_2$ **III₁—**
III₂-(11)

B.P. 110–111.5° at 765 mm. (1)
110° (2)

Note that the prod. of b.p. 180°, formerly (3) supposed to have been $\bar{C}$, is in fact (2) diallyl carbonate.

[For prepn. of $\bar{C}$ from allyl alc. (1:6145) with phosgene (3:5000) (yield 37% (1)) (4) (2) see indic. refs.; note that some diallyl carbonate, b.p. 166° at 730 mm. (2), is also formed (2).]

$\bar{C}$ in quinoline begins to decompose at 37° (5) (6) presumably into CO_2 + allyl chloride (3:7035) although this is not specifically stated.

[For reaction of $\bar{C}$ with diethylene glycol (1:6525), triethylene glycol (1:6538), etc., see (7).]

3:7487 (1) Schving, Sabetay, *Bull. soc. chim.* (4) **43**, 858 (1928). (2) Fierz-David, Müller, *J. Chem. Soc* **125**, 26 (1924) (3) Thiele, Dent, *Ann.* **302**, 262 (1898). (4) Schving, French 34,412, June 18, 1929, *Cent* **1929**, II 2829. (5) Carré, *Bull. soc. chim.* (5) **3**, 1072 (1936) (6) Carré, Passedouet, *Compt. rend.* **201**, 899 (1935). (7) Muskat, Strain (to Pittsburgh Plate Glass Co), U.S 2,370,565, Feb. 27, 1945; *C.A.* **39**, 4526 (1945).

3:7490 2-CHLORO-2-METHYLPENTANE $C_6H_{13}Cl$ **Beil. I - 148**
(Dimethyl-*n*-propyl-carbinyl chloride) **I₁-(53)**
I₂-(111)

$$CH_3.CH_2.CH_2{-}\underset{Cl}{\overset{CH_3}{C}}{-}CH_3$$

B.P.

110–111° dec. at 734 mm. (1)	D_4^{20} = **0.863 (1)**		
110–113° (2)		n_D^{20} = **1.4126 (3); cf. (1)**	
64.5–64.7° at 160 mm. (3)	D_4^{15} = **0.8678 (2)**		
50–53° at 41 mm. (4)		$n_D^{16.5}$ = **1.4176**	**(2)**
36–37° at 15 mm. (5)			

C̄ decomposes considerably if distd. at ord. press. (3).

[For prepn. (93% yield (2)) from paraldehyde (1:0170) + n-propyl alc. (1:6150) + dry HCl see (2) (3).]

C̄ on stdg. polymerizes to dark tarry residue (2).

[C̄ on bromination yields α,β-dibromoethyl n-propyl ether (3).]

C̄ on shaking with aq. yields acetaldehyde (1:0100), n-propyl alc. (1:6150) + HCl.

3:7525 (1) Gauthier, *Ann. chim.* (8) **16**, 312 (1909). (2) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077–4079 (1931). (3) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* **52**, 3399–3400 (1930).

3:7530 2-CHLOROHEXENE-1 $C_6H_{11}Cl$ Beil. S.N. 11

$$CH_3.CH_2.CH_2.CH_2-\underset{}{\overset{Cl}{\overset{|}{C}}}=CH_2$$

B.P.

113° at 740 mm. (1)		D_4^{25} = **0.8886** (1)	n_D^{25} = **1.4278** (1)
109.5–110.5° at 735 mm. (2)		**0.8872** (2)	**1.4187** (2)

[For prepn. of C̄ from hexyne-1 (1:8055) with dry HCl + $BiCl_3$ in C_6H_6 (20% yield (1) together with 40% yield 2,2-dichlorohexane (3:9342)) or with AcCl + $SnCl_4$ (15% yield (2) together with 37% 4-chloro-octen-3-one-2, b.p. 75–95° at 20 mm.) see (1) (2); for prepn. of C̄ (60.5% yield (1)) from 2,2-dichlorohexane (3:9342) with KOH in n-propyl alc. at 95° see (1).]

C̄ in CCl_4 + $SbCl_5$ treated with Cl_2 at 35–40° gives (1) (3) *cis*-1,2-dichlorohexene-1 (3:9330) (26.7% yield (1)) together with 25.4% 1,1,2,2-tetrachlorohexane (3:9332).

3:7530 (1) Hennion, Walsh, *J. Am. Chem. Soc.* **62**, 1367–1368 (1940). (2) Kroeger, Sowa, Nieuwland, *J. Org Chem.* **1**, 163–169 (1936). (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 450 (1940).

3:7535 3-CHLOROHEXENE-3 $C_6H_{11}Cl$ Beil. S.N. 11

$$CH_3.CH_2-\overset{Cl}{\overset{|}{C}}=CH.CH_2\,CH_3$$

B.P. 113.0–113.5° at 748 mm. (1) D_4^{25} = **0.8898** (1) n_D^{25} = **1.4320** (1)

Two geom. stereoisomers of C̄ are possible, but only this one is as yet recognized.

[For prepn. of C̄ from hexyne-3 (diethylacetylene) (1:8065) with AcCl + $SnCl_4$ see (1); (both *cis* and *trans* stereoisomers of 4-chloro-3-ethylhexen-3-one-2 are also formed).

3:7535 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163–169 (1936).

3:7540 n-PROPYL CHLOROFORMATE $C_4H_7O_2Cl$ Beil. III - 11
(n-Propyl chlorocarbonate) n-$C_3H_7.O.CO.Cl$ III_1-(6)
III_2-(10)

B.P. 114–115.5° at 768 mm. (1)		D_4^{20} = **1.0901** (1)	n_D^{20} = **1.40350** (4)
115.2 cor. (2) (3)			

C̄ reacts but slowly with cold aq., more rapidly on warming, yielding n-propyl alc. (1:6150) + CO_2 + HCl.

[For prepn. from n-propyl alc. (1:6150) + phosgene (3:5000) (42% yield (3)) see (2) (3).]

C̄ on htg. with $ZnCl_2$ yields (5) propylene, CO_2, + HCl; C̄ on warming with pyridine or quinoline dec. at 66° into n-propyl chloride (3:7040) + CO_2 (6) cf. (7).

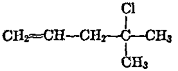
CHAPTER XVII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:7500–3:7999)

3:7500 4-CHLORO-4-METHYLPENTENE-1 $C_6H_{11}Cl$ **Beil. I - 217**
(2-Chloro-2-methylpentene-4) I_1—
(Allyl-dimethyl-carbinyl chloride) I_2—

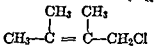


B.P. 109–114° sl. dec. (1)

[For prepn. of $\bar{C}$ from 2-methylpenten-4-ol-2 (allyl-dimethyl-carbinol) [Beil. I-445, I_2-(487)] with PCl_5 see (1).]

3:7500 (1) M. Saytzeff, A. Saytzeff, *Ann.* **185**, 156 (1877).

3:7520 1-CHLORO-2,3-DIMETHYLBUTENE-2 $C_6H_{11}Cl$ **Beil. S.N. 11**
(β,γ,γ-Trimethylallyl chloride)



B.P. 111–112° at 756 mm. (1) D_4^{19} = **0.8895 (1)** n_C^{19} = **1.4315 (1)**

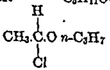
Note. $\bar{C}$ by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 3-chloro-2,3-dimethylbutene-1 (α,α,β-trimethylallyl chloride). The material described by (1) was regarded as $\bar{C}$; the isomer seems to be unrecorded.

[For prepn. of $\bar{C}$ (or its mixt. with 3-chloro-2,3-dimethylbutene-1) in 90% yield from 2,3-dimethylbutene-2 (tetramethylethylene) (1:8290) with $Cl_2 + NaHCO_3$ at 0° see (1).]

$\bar{C}$ on hydrolysis yields (1) a hexenol (regarded (1) as 2,3-dimethylbuten-1-ol-3 derived from the synionic isomer of $\bar{C}$), b.p. 116–118°, D_4^{17} = 0.835, n_C^{17} = 1.4248 (1).

3:7520 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939).

3:7525 α-CHLOROETHYL n-PROPYL ETHER $C_5H_{11}OCl$ **Beil. I - 607**
I_1—
I_2—



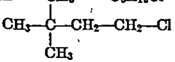
B.P. 112–115° at 731 mm. (1) D_4^{20} = **0.9322 (2)** n_D^{20} = **1.4013 (2)**
47.5° cor. at 40 mm. (2)

[$\bar{C}$ on passing over alkali (NaOH, K_2CO_3, soda-lime, etc.) at elevated temperatures (e.g., 700–750°) yields (6) butadiene-1,3.]

[$\bar{C}$ with boilg. satd. n-BuOH/KOH loses 1 HCl giving (64% yield (9)) 1-chlorobutene-1 (3:7110).]

3:7550 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223. (2) Kohlrausch, Köppl, *Monatsh.* **65**, 197 (1935). (3) Meyer, Petrenko-Kritschenko, *Ber.* **25**, 3308 (1892). (4) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* **61**, 940 (1939). (5) Muskat (to du Pont), U.S. 2,038,593, April 28, 1936; *Cent.* **1936**, II 3358. (6) Muskat (to du Pont), U.S. 2,070,609, Feb. 16, 1937; *Cent.* **1937**, II 2597. (7) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 893–896 (1937); *C.A.* **31**, 5755 (1937); *Cent.* **1938**, II 2575. (8) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4050–4052 (1930). (9) Henne, Hinkamp, *J. Am. Chem. Soc.* **67**, 1197 (1945).

3:7555 4-CHLORO-2,2-DIMETHYLBUTANE $C_6H_{13}Cl$ Beil. S.N. 10
(Neopentylcarbinyl chloride)



B.P. 115° (1) (2) D_4^{20} = **0.8670** (2) n_D^{20} = **1.4161** (1)
41° at 50 mm. (2) (3) **1.4160** (2) (3)

[For prepn. of $\bar{C}$ (60% yield) from corresp. alc. (neopentylcarbinol) (1:6219) with $SOCl_2$ + pyridine see (1); for prepn. of $\bar{C}$ from *ter*-butyl chloride (3:7045) + ethylene in presence of $AlCl_3$ (75% yield), $FeCl_3$ (57% yield), or $BiCl_3$ (6–30% yield) see (2).]

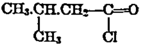
$\bar{C}$ with Mg + dry ether yields RMgCl which with oxygen yields (1) (2) neopentylcarbinol (1:6219) q.v.

Ⓓ Neopentylcarbinyl mercuric chloride ($C_6H_{13}HgCl$): m.p. 133–133.5° (1). [From RMgCl + $HgCl_2$ (1).]

Ⓓ γ,γ-Dimethyl-n-valeranilide: ndls. from dil. alc., m.p. 138–139° (2). [From $\bar{C}$ via conversion to RMgCl and reaction with phenyl isocyanate (2).]

3:7555 (1) Whitmore, Bernstein, *J. Am. Chem. Soc.* **60**, 2626–2628 (1938). (2) Schmerling, *J. Am. Chem. Soc.* **67**, 1152–1154 (1945). (3) Schmerling, *J. Am. Chem. Soc.* **67**, 1782–1783 (1945).

3:7560 ISOVALERYL CHLORIDE C_5H_9OCl Beil. II - 315
(β-Methyl-n-butyryl chloride) II_1-(137)
II_2-(277)



B.P.		D	n
[**117.9°** at 766 mm. (1)]		$D_4^{24.3}$ = **0.9854** (2)	$n_D^{24.3}$ = **1.41361** (2)
114.5–115.5° at 771 mm. (2)		D_4^{20} = **0.9887** (6)	n_D^{20} = **1.4157** (3)
115.5° at 741 mm. (3)		**0.9862** (3)	**1.41555** (6)
114.3–115.7° (4)		**0.9844** (1)	**1.41488** (1)
114.5–115.5° (5)			
***113.5–114.5°* at 725.7 mm.** (6)			

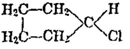
[For prepn. of $\bar{C}$ from isovaleric acid (1:1050) with PCl_3 (7) (8) (9), with PCl_3 + $ZnCl_2$ (79% yield (10)), with $SOCl_2$ (72% yield (10)) (1) (5) see indic. refs.; note that use of PCl_5 is inadvisable since the by-prod., $POCl_3$, boils too close to $\bar{C}$.]

[$\bar{C}$ htd. with K isovalerate yields (11) isovaleric anhydride [Beil. II-314, II_1-(137), II_2-(277)], b.p. 215.1–215.3° at 762 mm., 102–103° at 15 mm. (11), D_4^{20} = 0.9327, n_D^{20} = 1.4043 (12).]

Ⓓ *n*-Propyl *N*-phenylcarbamate (*n*-propyl carbanilate) [Beil. XII-321]: from $\bar{C}$ + excess aniline in ether, cryst. from alc., m.p. 57–59° (8).

3:7540 (1) Karvonen, *Ann. Acad. Sci Fennicae* **A-10**, No 4, 19 (1916); *Cent.* **1919**, III 808. (2) Roese, *Ann.* **205**, 227–230 (1880). (3) Hamilton, Sly, *J. Am Chem. Soc.* **47**, 436–437 (1925). (4) Dobrosserdow, *Cent.* **1911**, I 954. (5) Underwood, Baril, *J. Am. Chem. Soc.* **53**, 2201 (1931). (6) Carré, *Bull. soc. chim.* (5) **3**, 1069 (1936). (7) Fry, *J. Am. Chem. Soc.* **36**, 260–261 (1914). (8) Roemer, *Ber.* **6**, 1103 (1878).

3:7545 CHLOROCYCLOPENTANE (Cyclopentyl chloride)



C_5H_9Cl Beil. V - 19, V_1-(4), V_2-(4)

B.P. 114–115.5° cor. (1)		D_4^{20} = **1.0051** (1) (2)	n_D^{20} = **1.4510** (1)
114–115° at 748 mm. (2)		**1.005** (4)	**1.4509** (2)
114.1–114.9° (3)			
114° (4)			

[For prepn. of $\bar{C}$ from cyclopentanol (1:6412) with boilg. conc. HCl + $CaCl_2$ (87% yield (5)) (6), or with conc. HCl at 110° (87% yield (2)) (1) (7) (8), or with PCl_3 at 0° (3) (4) see indic. refs.] [Some cyclopentene (1:8037), b.p. 34°, may also be formed but is readily sepd. by distn.] [For prepn. of $\bar{C}$ from cyclopentane (1:8400) with Cl_2 see (13).]

$\bar{C}$ over $BaCl_2$ at 300–400° at 15–20 mm. yields (9) cyclopentene (1:8037).

[$\bar{C}$ with C_6H_6 + $AlCl_3$ gives (54% yield (10)) phenylcyclopentane (cyclopentylbenzene), b.p. 217°, D_4^{20} = 0.9474, n_D^{20} = 1.5280 (10); for reactn. of $\bar{C}$ with 2-methylpyridine (α-picoline) see (11); for reactn. of $\bar{C}$ with Na_2SO_3 at 200° see (4).]

$\bar{C}$ with Mg in dry ether gives (1) (2) (5) (7) cyclopentyl MgCl; this with CO_2 gives (1) (7) cyclopentanecarboxylic acid [Beil. IX-6], b.p. 215.5–216° cor., D_4^{20} = 1.0510, n_D^{18} = 1.4534 (1) (amide, lfts. from MeOH, m.p. 179° cor. (1), 178° (12)).

Ⓓ Cyclopentyl mercuric chloride C_5H_9HgCl: m.p. 108.5° (4). [The method of formn. of this deriv. is not stated but is presumably from RMgCl + $HgCl_2$.]

3:7545 (1) Zelinskiĭ, *Ber.* **41**, 2627–2628 (1908). (2) Zelinskiĭ, Mikhlina, Eventova, *Ber.* **66**, 1422–1426 (1933) (3) Kohlrausch, Reitz, Stockmair, *Z. physik. Chem.* **B-32**, 235 (1936). (4) Turkiewicz, Pilat, *Ber.* **71**, 284–285 (1938). (5) Pilat, Turkiewicz, *Ber.* **72**, 1527–1531 (1939). (6) Yarnall, Wallis, *J. Org. Chem.* **4**, 287 (1939). (7) Neunhoffer, Schluter, *Ann.* **526**, 70 (1936). (8) Canals, Mousseron, Granger, Gastaud, *Bull. soc. chim.* (5) **4**, 2048 (1937). (9) Badische Anilin u. Sodafabrik, Ger. 255,538, Jan. 3, 1913, *Cent.* **1913**, I 477. (10) Zelinskiĭ, Titz, *Ber.* **64**, 185 (1931).

(11) Tschitschibabine, *Bull. soc. chim.* (5) **5**, 435 (1938). (12) Nenitzescu, Cantuniari, *Ber.* **65**, 811 (1932). (13) Bailey, McAllister (to Shell Development Co.), U.S. 2,342,072, Feb. 15, 1944; *C A.* **38**, 4621 (1944).

3:7550 1,1-DICHLOROBUTANE $CH_3.CH_2.CH_2.CHCl_2$ $C_4H_8Cl_2$ Beil. I - 119

(*n*-Butylidene (di)chloride) I_1— I_2—

B.P. 114.5–115° at 763 mm. (1)		D_4^{20} = **1.0863** (7)	n_D^{20} = **1.4355** (7)
113.8–113.9° (2)			
113–115° (3) (7)			

[For prepn. (47% yield (4)) from *n*-butyraldehyde (1:0130) by actn. of PCl_5 (39% yield (9)) see (1) (2) (3) (9); for formn. from butane by chlorination see (5) (6); for formn. from *n*-butyl chloride (3:7160) on chlorination see (7) (8).]

[C̄ with equal wt. ethyl mercaptan gives (34% yield (33)) 1,3-*bis*-(ethylmercapto)-propanone-2, b.p. 117–121° at 15 mm. (33) (corresp. semicarbazone, m.p. 98–99°), but C̄ with large excess ethyl mercaptan (4 wt. pts.) gives *also* 1,2,2,3-tetra(ethylmercapto)-propane, oil (33). — C̄ (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH yields (34) 1,3-*bis*-(benzylmercapto)propanone-2, oil, which on oxidn. in acid soln. with $KMnO_4$ gives the corresp disulfone, ndls. from alc., m.p. 182° (34).] — [For reactn. of C̄ with alk. sulfides and/or polysulfides in prepn. of resins see (37).]

C̄ with KI even at room temp. (7) yields 1,3-diiodoacetone, pr. from acetone, m.p. 61°.

[For reaction of C̄ with MeMgBr as means of prepn. of *sym.*-dichloro-*ter*-butyl alcohol (3:5977) see the latter.]

[C̄ with excess conc. aq. or liq. HCN in alc. at 30° for 12 hrs. (11) cf. (35) or with 25% HCN in pres. of a little NH_4OH (36) yields β,β′-dichloro-α-hydroxyisobutyronitrile (not isolated), which on hydrolysis with HCl (11) (35) (36) gives the corresp. acid, β,β′-dichloro-α-hydroxyisobutyric acid, m.p. 91–92° (11).]

[C̄ with diazotized aniline in pres. of NaOAc yields (3) 1,3-dichloro-1-(benzeneazo)-propanone-2, red-or. cryst. from hot alc., m.p. 156–157° (3); for corresp. homologs using diazotized *o*-toluidine or *p*-toluidine see (3).]

[C̄ with equiv. molar quant. thioacetamide in acetone or alc. followed by htg. with $ZnCl_2$ (38) (39) gives 4-(chloromethyl)-2-methylthiazole hydrochloride (free base is oil, b.p. 65–67° at 3 mm. (38) (39)); for polymerization of this prod. by htg. see (38). — C̄ with thiobenzamide in acetone followed by htg. of resultant intermediate with HCl in acetone gives 4-(chloromethyl)-2-phenylthiazole hydrochloride (yields: 80–81% (40) (41)) (corresp. free base, m.p 51° (40), 48.2–51.2° cor. (41)); for reactns. of this prod. see (41). — For analogous reactn. of C̄ with many other substituted thiobenzamides to give corresp. substituted thiazoles see (40) (39).]

[C̄ with equiv. molar amt. carbamyl chloride in dry ether at room temp. for 15 min. is claimed (2) to yield β,β′-dichloroisopropyl carbamate ("Aleudrin"), white cryst. from alc., m.p. 80–81° (2); C̄ with 2 molar equivs. of carbamyl chloride similarly treated is claimed (2) to yield β,β-dichloroisopropyl allophanate, cryst. from 60% alc., m.p. 182° (2); note, however, that in view of the facts that the C̄ used in the cited work was obtd. from 1,3-dichloropropanol-2, that the b.p.'s of this precursor and C̄ are almost identical, and that the C̄ employed was purified only by distillation, the indicated esters may have been due to the presence of unoxidized starting material.]

Ⓓ **1,3-Dichloropropanone-2 semicarbazone:** m.p. 120° (23). [Note that this prod. is very sensitive to heat (care in recrystn. from aq. or C_6H_6) and is also changed by stdg. in solution (23).]

Ⓓ **1,3-Dichloropropanone-2 4-(*p*-bromophenyl)semicarbazone:** ndls. from alc., m.p. 196° cor. dec. (42). [From C̄ + 4-(*p*-bromophenyl)semicarbazide in alc. refluxed for 12 hrs. (42).]

Ⓓ Condensation product ($C_{17}H_{19}O_4N_3SCl_2$) of C̄ with *N*-methyl-3-(carbohydrazido)-pyridinium *p*-toluenesulfonate: cryst. from 1:1 alc./ether, m.p. 115° cor. (43). [From C̄ with nicotinic acid hydrazide metho-*p*-toluenesulfonate in abs. alc. on refluxing for 15 mins. (43).]

3:0563 (1) Markownikow, *Ann.* **208**, 353–358 (1881). (2) Sen, Barat, *J. Indian Chem. Soc.* **2**, 77–81 (1925). (3) Favrel, *Bull. soc. chim.* (5) **1**, 983–986, 989 (1934). (4) Posner, Rohde, *Ber.* **42**, 3237–3242 (1909). (5) Edwards, Evans, Watson, *J. Chem. Soc.* **1937**, 1944. (6) Glutz, Fischer, *J. prakt. Chem.* (2) **4**, 54–55 (1871). (7) von Hoerman, *Ber.* **13**, 1706–1709 (1880). (8) Cloez, *Ann. chim.* (6) **9**, 167–170 (1886). (9) Erlenbach, *Ann.* **269**, 46–48 (1892). (10) Conant, Quayle, *Org. Syntheses*, Coll. Vol. **1** (2nd ed.), 211–213 (1941); Coll. Vol. **1** (1st ed.), 206–207 (1932); **2**, 13–15 (1922).

[C̄ with Cl_2 in CCl_4 yields (8) α-chloroisovaleryl chloride (3:8144), b.p. 148–149° (together with some β-chloroisovaleryl chloride).]

[C̄ on cat. hydrogenation using Pd as specified (13) gives 95% yield isovaleraldehyde (1:0140), b.p. 92° (13) (use of PtO_2 gives (14) only small yield).]

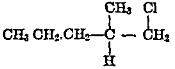
[For reactn. of C̄ with acetylene + $AlCl_3$ in pet. eth. at 0–5°, yielding on treatment with aq. β-chlorovinyl isobutyl ketone, b.p. 63–65°, see (15); with cyclohexene + $AlCl_3$ in cyclohexane yielding cyclohexyl isobutyl ketone, b.p. 216–219°, $D_4^{20} = 0.8867$, $n_D^{20} = 1.58155$, see (16); with sodium azide in benzene yielding isobutyl isocyanate see (17).]

C̄ on hydrolysis yields isovaleric acid (1:1050), b.p. 176.5°. — For the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see isovaleric acid (1:1050).

3:7560 (1) Leimu, *Ber.* **70**, 1049 (1937). (2) von Auwers, Schmidt, *Ber.* **46**, 474 (1913). (3) Martin, Partington, *J. Chem. Soc.* **1936**, 162. (4) Kohlrausch, Pongratz, *Z. physik. Chem.* B-**22**, 382 (1933). (5) Bardan, *Cent* **1932**, II 354. (6) Brühl, *Ann.* **203**, 24 (1880). (7) Béchamp, *Jahresber.* **1856**, 429. (8) Michael, *Ber.* **34**, 4055–4056 (1901). (9) Scheuble, Ger. 251,806, Oct. 8, 1912; *Cent.* **1912**, II 1503. (10) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III, 97–103 (1933).

(11) Verkade, *Rec. trav. chim.* **36**, 197 (1916). (12) Tromp, *Rec. trav. chim.* **41**, 299 (1921). (13) Froschl, Danoff, *J. prakt. Chem.* (2) **144**, 221–222 (1935). (14) Grignard, Mingasson, *Compt. rend.* **185**, 1176 (1927). (15) Nelles, Baeyer (to I.G.), Brit 461,080, March 11, 1937; Ger. 642,147, Feb. 25, 1937, *Cent.* **1937**, II 2597, *C.A.* **31**, 4676 (1937). (16) Nenitzescu, Cioranescu, *Ber.* **69**, 1823 (1936). (17) Naegeli, Grüntuch, Lendorff, *Helv. Chim. Acta* **12**, 247–248 (1929).

3:7563 *d,l*-**1-CHLORO-2-METHYLPENTANE** $C_6H_{13}Cl$ Beil. I — I_1— I_2-(111)



B.P. 110–120° (1)

[For prepn. of C̄ from levorotatory 2-methylpentanol-1 with PCl_5 in $CHCl_3$ or from dextrorotatory 2-methylamylamine with NOCl see (1).]

3:7563 (1) Levene, Mikesa, *J. Biol Chem.* **84**, 579–580 (1929).

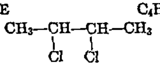
3:7565 *d,l*-**3-CHLORO-2-METHYLPENTANE** $C_6H_{13}Cl$ Beil. I - 148
(Ethyl-isopropyl-carbinyl chloride) I_1— I_2-(111)

B.P. 115–116.5° dec. at 752 mm. (1)

[For prepn. of C̄ from 2-methylpentanol-3 (1:6194) with PCl_5 see (1).]

3:7565 (1) Grigorowitsch, Pavlov, *J. Russ. Phys.-Chem. Soc.* **23**, 166 (1891).

3:7580 ***meso*-2,3-DICHLOROBUTANE** $C_4H_8Cl_2$ Beil. I —
(*meso*-β-Butylene dichloride) I_1—
I_2-(82)



B.P.		F.P.		
116.0°	(1) (2)	−80.4° (1)	D_4^{25} = 1.1023 (6)	
115.9°	at 760 mm. (3)			n_D^{25} = 1.4395 (6)
115.5–116.5° cor.	at 746 mm. (4)			1.4392 (6)
114–116°	(5)			1.4386 (6)
113.14°	at 746 mm. (6)			1.4385 (6)
49.52°	at 80 mm. (6)		D_4^{20} = 1.1134 (5)	
49.0–50.5°	at 80 mm. (7)		1.1067 (2)	
49.4–49.7°	at 80 mm. (6)			n_D^{20} = 1.4413 (2)
48.5–49.0°	at 80 mm. (6)			1.443 (5)

[*See also d,l-2,3-dichlorobutane* (3:7615).]

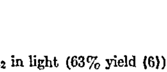
[For prepn. of C̄ from *trans*-butene-2 with Cl_2 in light (63% yield (6)) (7) cf. (5) indic. refs.; for formn. of C̄ from *d,l-erythro*-3-chlorobutanol-2 (3:8004) (16% yield (6)) or from (+) *threo*-3-chlorobutanol-2 (3:8002) (15% yield (6)) with $SOCl_2$ see (6) (note that from *d,l-erythro*-3-chlorobutanol-2 with PCl_5 in $CHCl_3$ a mixt. of C̄ + its *d,l*-isomer (3:7615) is obtd. (6)); for formn. of C̄ from *d,l*-2-chlorobutane (3:7125) with Cl_2 in light (42.7% yield) see (2).]

[C̄ with Cl_2 (slight excess) in dark at −17° gives (5) 36.5% 1,2,3-trichlorobutane (3:5935) + 18% 2,2,3-trichlorobutane (3:5680).]

[C̄ with alc. KOH gives same results as does the *d,l*-isomer (3:7615) (3).]

3:7580 (1) Timmermans, *Bull soc. chim. Belg.* **36**, 504 (1927). (2) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 663–666 (1937); *Cent* **1937**, II 372; *C.A.* **31**, 5754 (1937). (3) Nave, *Bull. soc. chim. Belg.* **39**, 435–439 (1930). (4) Lucas, Simpson, Carter, *J. Am. Chem. Soc.* **47**, 1467 (1925). (5) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1553–1558 (1936); *Cent.* **1937**, I 3785; *C.A.* **31**, 2165 (1937). (6) Lucas, Gould, *J. Am. Chem. Soc.* **63**, 2541–2545 (1941). (7) Taufen, Murray, Cleveland, *J. Am. Chem. Soc.* **65**, 1131–1132 (1943).

3:7585 **3-CHLORO-3-METHYLPENTANE** $C_6H_{13}Cl$ Beil. I - 149
(Diethyl-methyl-carbinyl chloride) I_1-(54)
I_2-(112)



B.P.		B.P. (*contd.*)			
116°	(1)	85°	at 280 mm. (5)	D_4^{20} = 0.8900 (4)	
115–118°	(2)	69.5°	at 160 mm. (6)		n_D^{20} = 1.4210 (3)
115–117°	(3)	68–69°	at 160 mm. (7)		1.4208 (7)
117–118° at 750 mm.	(4)	35°	at 25 mm. (4)		1.4202 (6)
111° at 761 mm.	(5)			D_4^{14} = 0.8893 (1)	
				0.878 (3)	
					n_D^{17} = 1.4215 (3)

[For density of C̄ at 0°, 15°, 25°, 50°, and 65° together with parachors at 0°, 25°, and 50° see (9).]

[For prepn. of C̄ from corresp. alc., diethyl-methyl-carbinol (3-methylpentanol-3) (1:6189), with PCl_5 (8), HCl gas (1) (2) at 0° (5) or 10–15° (59% yield (7)) see indic. refs.

with diphosgene (3:5515) see (4); for formn. from 3-methylpentene-2 (1:8260) + conc. HCl see (3); for formn. (together with other products) during reaction of 2-ethylbutanol-1 (1:6223) with HCl + $ZnCl_2$ see (6).]

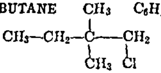
$\bar{C}$ with Mg in dry ether yields (7) corresp. RMgCl.

Ⓓ *Diethyl-methyl-acetanilide: m.p. 86.5–88.5° (6). [From $\bar{C}$ via conversion to RMgCl* and reaction with phenyl isocyanate (6).]

3:7585 (1) Schreiner, *J. prakt. Chem.* (2) **82**, 295 (1910). (2) Gilman, Schulze, *J. Am. Chem. Soc.* **49**, 2330 (1927) (3) Nasarow, *Ber.* **70**, 621 (1937). (4) Nekrassow, Melnikow, *J. prakt. Chem.* (2) **127**, 217–218 (1930). (5) Favorskii, Zalesskii-Kibardine, *Bull soc. chim.* (4) **37**, 1230 (1925). (6) Whitmore, Karnatz, *J. Am Chem Soc* **60**, 2535 (1938). (7) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1561 (1933). (8) Butlerow, *Bull soc. chim.* (2) **5**, 23–24 (1866). (9) Quayle, Owen, Beavers, *J. Am Chem. Soc.* **61**, 3107–3111 (1939).

3:7590 1-CHLORO-2,2-DIMETHYLBUTANE $C_6H_{13}Cl$ Beil. S.N. **10**

(*ter*-Amyl-carbinyl chloride; neohexyl chloride)



B.P. 116.1° at 735 mm. (1) n_D^{20} = **1.4200 (1)**

113.5–115° (2) **1.4190 (2)**

[For prepn. of $\bar{C}$ from 2,2-dimethylbutane (neohexane) (1:8510) with Cl_2 in the cold see (2).]

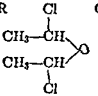
[$\bar{C}$ with Na yields (1) a mixt. of 4 compounds: 11.8% 1,1,2-trimethylcyclopropane, b.p. 56.5–57° at 735 mm., D_4^{20} = 0.6967, n_D^{20} = 1.3880; 7.8% 2,2-dimethylbutene-3 (*ter*-butylethylene) (1:8225); 27.1% 2,2-dimethylbutane (neohexane) (1:8510); and 4.3% normal coupling prod, 3,3,6,6-tetramethyloctane, b.p. 125° at 140 mm., n_D^{20} = 1.423.]

3:7590 (1) Whitmore, Carney, *J. Am. Chem. Soc.* **63**, 2633–2635 (1941). (2) Whitmore, Bernstein, Mixon, *J. Am. Chem. Soc.* **60**, 2539 (1938).

3:7595 α,α′-DICHLORODIETHYL ETHER $C_4H_8OCl_2$ Beil. I - 607

(*bis*-(α-Chloroethyl) ether) I_1—

I_2—



B.P. 116–117° (1) (2) D_4^{25} = **1.106 (3)** n_D^{25} = **1.4186 (3)**

112.5–114° (3)

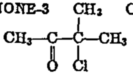
Colorless liq. at first immiscible with aq. but grad. hydrolyzing (especially on warming) to acetaldehyde (1:0100) and HCl (1) (2).

[For prepn. of $\bar{C}$ from acetaldehyde (1:0100) with dry HCl gas see (2) (1).]

For identification hydrolyze $\bar{C}$ to acetaldehyde (1:0100) (3), derivatize the latter, e.g., via the *p*-nitro- or 2,4-dinitrophenylhydrazones.

3:7595 (1) Lieben, *Ann.* **106**, 337 (1858). (2) Geuther, Laatsch, *Ann.* **218**, 16–18 (1883). (3) Gebauer-Fuelnegg, Moffett, *J. Am. Chem. Soc.* **56**, 2009 (1934).

3:7597 2-CHLORO-2-METHYLBUTANONE-3 C_5H_9OCl Beil. S.N. 87



B.P. 117.2° (1) D_4^{20} **= 1.0083 (1)** n_D^{20} **= 1.42044 (1)**

[For prepn. of $\bar{C}$ from 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) with SO_2Cl_2 in cold (84% yield (1)) or with Cl_2 by vapor-phase chlorination (2) see indic. refs.]

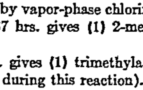
$\bar{C}$ with 20% aq. Na_2CO_3 refluxed for 37 hrs. gives (1) 2-methylbutanon-3-ol-2 [Beil. I-832, I_1-(422), I_2-(873)], b.p. 143° (1).

$\bar{C}$ with 40% aq. NaOH refluxed 20 hrs. gives (1) trimethylacetic acid (1:0410), b.p. 163°, m.p. 35° (1) (note structural change during this reaction).

$\bar{C}$ with aq. KCN in cold for 1 hr. gives (1) 2,3-dimethyl-2,3-epoxy-*n*-butyronitrile, b.p. 157.8° at 747 mm., $D_4^{20} = 0.9314$, $n_D^{20} = 1.41334$ (1).

3:7597 (1) Delbaere, *Bull. soc. chim. Belg.* **51**, 1–10 (1942); *Cent.* **1942**, II 763–764; *C.A.* **37**, 5018 (1943). (2) Justoni, *Chimica e industria (Italy)* **24**, 195–201 (1942); *Cent.* **1943**, I 1659.

3:7598 *d,l*-3-CHLOROBUTANONE-2 C_4H_7OCl Beil. I - 669
(α-Chloroethyl methyl ketone) I_1-(348)
I_2-(731)



B.P.			B.P. (*contd.*)			
117–119° (1)	**at 760 mm.**	**(8)**	**49–50°**	**at 70 mm.**	**(6)**	D_-^0 **= 1.032 (5) (15)**
114–117°	**at 760 mm.**	**(2)**	**46°**	**at 40 mm.**	**(10)**	
116–117°		**(3)**	**32°**	**at 40 mm.**	**(4)**	
116°	**at 770 mm.**	**(4)**	**40–41°**	**at 30 mm.**	**(2)**	
115°	**at 758 mm.**	**(5) (15)**	**33–34°**	**at 30 mm.**	**(7)**	
115°		**(6)**	**26°**	**at 18 mm.**	**(4)**	
114–115°		**(7) (16)**				
114°		**(9)**				

[*See also* 1-*chlorobutanone*-2 (3:8012).]

Liquid with penetrating odor. — Insol. aq., eas. sol. alc., ether.

[For prepn. of $\bar{C}$ from ethyl methyl ketone (butanone-2) (1:5405) with Cl_2 in pres. of $CaCO_3$ + aq. (yields of $\bar{C}$ about 75% always accompanied by 25% of the isomeric 1-chlorobutanone-2 (3:8012)) see (2) (6) (7) (10) cf. (11); with Cl_2 as vapor-phase chlorination see (12) (13) (14); with Cl_2 diluted with dry CO_2 see (15) (4); with Cl_2 in sunlight see (5) (16); with SO_2Cl_2 in sunlight see (5) (16) (17) cf. (11); with *N*-chlorourea in dil. AcOH see (1) (8); for prepn. of $\bar{C}$ from acetyl chloride (3:7065) with ethylene over activated carbon at 100° and 50 atm. see (18) (note that acetyl chloride + ethylene + $AlCl_3$ at 0° gives 4-chlorobutanone-2 (3:7640) q.v.); for prepn. of $\bar{C}$ from 2-chlorobutene-2 (3:7105) with Cl_2 + aq. + CCl_4 (65% yield) see (3).]

[$\bar{C}$ on reduction using yeast (20) gives levorotatory 3-chlorobutanol-2, b.p. 139° (cf. 3:8000), but with Zn + HCl (15) $\bar{C}$ yields butanone-2 (1:5405).]

$\bar{C}$ on oxidn. with conc. HNO_3 (5) (16) (20) yields α-chloropropionic acid (3:6125).

$\bar{C}$ on hydrolysis with aq. in s.t. at 150° for 6–8 hrs. (15), or $\bar{C}$ with alc. alk. (15) or MeOH/KOH (21) in cold, gives (84% yield (21)) butanone-2-ol-3 (acetyl-methyl-carbinol) (acetoin)

(1:5448) (as consequence of latter reactn. $\bar{C}$ reduces Tollens' reagt. or Fehling's soln. in cold).

$\bar{C}$ with satd. aq. $NaHSO_3$ soln. yields (15) a $NaHSO_3$ addn. cpd.

[$\bar{C}$ with conc. aq. KCN at 0° for 1 hr. gives (80% yield (21)) 2,3-epoxy-2-methyl-*n*-butyronitrile (*α*-cyano-*α*,*β*-dimethyl-ethylene oxide), b.p. 145°, $D_4^{20} = 0.9540$, $n_D^{20} =$ 1.4079 (21); $\bar{C}$ with alc. KCN gives (21) a mixt. consisting mainly of the above prod. together with a little *α*-methylacetoacetonitrile [Beil. III_2-(433)], b.p. 182–184° at 745 mm. with slight decompn. (22), b.p. 78° at 19 mm. (22), 68–70° at 12 mm. (23). (Note that the above represents a correction of the earlier views (5) (16) (24).)]

[$\bar{C}$ with conc. aq. $(NH_4)_2SO_3$ at 70° yields (9) butanone-2-sulfonic acid-3.—$\bar{C}$ with NaN_3 in aq. contg. AcOH yields (10) 3-azidobutanone-2, oil, b.p. 46° at 2 mm.]

[$\bar{C}$ with Na in abs. ether gives (15) by bimolecular coupling 3,4-dimethylhexanedione-2,5 [Beil. I-798, I_1-(409), I_2-(847)], b.p. 210° (15), 82° at 11 mm.; note therefore that sodium must not be used for drying $\bar{C}$ cf. (24).]

[$\bar{C}$ with triethyl orthoformate (1:3241) in abs. alc. in pres. of NH_4Cl as cat. gives (70% yield in 10 days but in absence of NH_4Cl only 39% (24)) *α*-chloroethyl methyl ketone diethylacetal, b.p. 80–84° at 36 mm., $D_4^{20} = 0.9773$ (24).]

[$\bar{C}$ with ethyl sodio-acetoacetate in abs. ether (4) or abs. alc. (25) (26) (24) gives (yields: 45–60% (24), 27–28% (26)) the expected ethyl *α*,*β*-diaceto-*n*-butyrate [Beil. III-757, III_1-(265), III_2-(468)], b.p. 150° at 28 mm. (25), 121–124° at 11 mm. (26). — $\bar{C}$ with ethyl acetoacetate (1:1710) + aq. NH_4OH + NH_3 gas htd. for 1 hr. gives (26% yield (4)) 3-carbethoxy-2,4,5-trimethylpyrrole [Beil. XXII-31, $XXII_1$-(497)], yel. cryst. from alc. or pet. eth., m.p. 101.5–102.5° (4), 104–105° (27), also obtd. from the above ethyl *α*,*β*-diaceto-*n*-butyrate with conc. aq. NH_4OH on warming (4). — $\bar{C}$ with *methyl* acetoacetate (1:1705) + conc. aq. NH_4OH in the cold gives (4) methyl *β*-aminocrotonate, m.p. 82–84° (4), which only on htg. condenses with the ester to give 3-carbomethoxy-2,4,5-trimethylpyrrole [Beil. XXII-31], cryst. from dil. alc., m.p. 124.5–126° (4) — $\bar{C}$ with *methyl* acetoacetate (1:1705) + CH_3NH_2 (33% in aq.) refluxed for some hours gives only very small yield (28) of 3-carbomethoxy-1,2,4,5-tetramethylpyrrole, cryst. from lgr., m.p. 101° (28).]

[$\bar{C}$ with diethyl acetonedicarboxylate (1:1772) in dry ether at −15° treated with NH_3 gas gives (10.7% yield (29)) 2-carbethoxymethyl-3-carbethoxy-4,5-dimethylfuran, b.p. 110–115° at 0.2 mm. (29).]

[For condens. of $\bar{C}$ with various phenols and phenol ethers see (30).]

[$\bar{C}$ with alc. NH_3 gives (15) in the cold the difficultly isolatable 3-aminobutanone [Beil. IV-319, IV_1-(452)], but on warming this condenses bimolecularly yielding (15) (8) tetramethylpyrazine [Beil. XXIII-99, $XXIII_1$-(28)], ndls. with $3H_2O$ from aq., m.p. 74–77°, but aq. lost in desic. to anhydrous prod., m.p. 86° (8) (corresp. picrate, m.p. 194–195° (31)). — $\bar{C}$ with aniline (2 moles) gives (15) on refluxing 2,3-dimethylindole [Beil. XX-319, XX_1-(130)], m.p. 107–109° (15).]

[$\bar{C}$ with thioformamide in abs. alc. for 4 days at 0° gives (22% yield (17)) 4,5-dimethylthiazole, b.p. 81–83° at 59 mm. (17) (corresp. picrate, cryst. from alc., m.p. 186–187° (17)). — $\bar{C}$ with NH_4 dithiocarbamate in abs. alc. refluxed ½ hr. gives (40% yield (17)) 2-mercapto-4,5-dimethylthiazole, cryst. from EtOAc, m.p. 163.5–163.8° (17). — $\bar{C}$ with benzamide + powd. $CaCO_3$ htd. at 110–120° for 10 hrs. gives (24% yield (32)) 4,5-dimethyl-2-phenyloxazole [Beil. $XXVII_1$-(219)], m.p. 50°, b.p. 128–130° at 5 mm. (32). — $\bar{C}$ with thiobenzamide + NaOAc htd. in abs. alc. gives (65% yield (32)) 4,5-dimethyl-2-phenylthiazole, b.p. 126–128° at 6 mm. (32).]

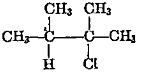
Ⓓ **3-Chlorobutanone-2 semicarbazone:** m.p. 148°, or on slow htg. 143–145° dec. (33), 127° (1).

3:7598 (1) Béhal, Detoeuf, *Compt. rend.* **153**, 1230 (1911). (2) Kling, *Bull. soc. chim.* (3) **33**, 325–326 (1905); *Ann. chim.* (8) **5**, 537–539 (1905). (3) Groll, Hearne (to Shell Development Corp.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* **1937**, I 4155; *C.A.* **31**, 419 (1937); Brit. 437,573, Nov. 28, 1935; French 787,529, Sept. 24, 1935; *Cent.* **1936**, II 2227. (4) Korschun, *Ber.* **38**, 1125–1129 (1905). (5) van Reymenant, *Bull. acad. roy. Belg.* **1900**, 724–742; *Cent.* **1901**, I 95. (6) Justoni, *Chimica e industria* (*Italy*) **24**, 89–94 (1942); *Cent.* **1943**, I 383. (7) Blaise, *Bull. soc. chim* (4) **15**, 733 (1914). (8) Godchot, Mousseron, *Bull. soc. chim.* (4) **51**, 356 (1932). (9) Backer, Strating, Zuithoff, *Rec. trav. chim.* **55**, 761–764 (1936). (10) Forster, Fierz, *J. Chem. Soc.* **93**, 675 (1908).

(11) Kolshorn, *Ber.* **37**, 2474–2475 (1904). (12) Justoni, *Chimica e industria* (*Italy*), **24**, 195–201 (1942); *Cent.* **1943**, I 1659. (13) Calkins (to B. F. Goodrich Co.), U.S. 2,120,392, June 14, 1938; *Cent.* **1939**, I 251; *C.A.* **32**, 5854 (1938). (14) I.G., French 813,131, May 26, 1937; *Cent.* **1937**, II 2071. (15) Démètre-Vladesco, *Bull. soc. chim.* (3) **6**, 404–415, 807–829 (1891). (16) Henry, *Bull. acad. roy. Belg.* **1900**, 57–63; *Cent* **1900**, I 1123. (17) Buchman, Reims, Sargent, *J. Org. Chem.* **6**, 767–769 (1941). (18) Frolich, Wiezevich (to Standard Oil Dev. Co.), U.S. 2,006,198, June 25, 1935, *Cent.* **1936**, I 2827; *C.A.* **29**, 5457 (1935). (19) Santomauro, *Biochem.* [illegible] 151, [illegible]) N. V. de Bataafsche Petroleum Maatschappij, French [illegible] 391 (1939); *Rend. ist. lombardo sci.* **71**, 407–424 (1938); *C.A.* **34**, 3268 (1940). (22) Mohr, *J. prakt. Chem.* (2) **90**, 199–200 (1914). (23) von Braun, Rudolph, *Ber* **67**, 1770 (1934). (24) Youtz, Perkins, *J. Am. Chem. Soc.* **51**, 3512 (Note 5); 3514 (1929). (25) Korschun, Roll, *Gazz. chim. ital.* **41**, I 188 (1911). (26) Willstätter, Clarke, *Ber.* **47**, 307 (1914). (27) Knorr, Hess, *Ber.* **44**, 2762 (1911). (28) Korschun, Roll, *Bull. soc. chim.* (4) **33**, 1107–1108 (1923). (29) Reichstein, Zschokke, Syz, *Helv. Chim. Acta* **15**, 1115–1116 (1932). (30) Curd, Robinson, *J. Chem. Soc* **1933**, 714–720, 1178–1179.

(31) Piloty, *Ber.* **43**, 496 (1910). (32) Friedman, Sparks, Adams, *J. Am. Chem. Soc.* **59**, 2263 (1937). (33) Blaise, *Bull soc. chim.* (4) **17**, 426 (1915).

3:7600 2-CHLORO-2,3-DIMETHYLBUTANE $C_6H_{13}Cl$ Beil. I - 151
(Dimethyl-isopropyl-carbinyl chloride) I_1—
I_2—

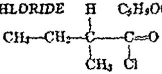


B.P. 118°	(1)		
117–119°	(2)	$D_-^{22} = $ **0.8769**	(2)
112° at 749 mm.	(3)		
68° at 185 mm.	(6)	$D_-^{19} = $ **0.8784**	(3)

Ⓓ 2,3-Dibromo-2,3-dimethylbutane: m.p. 173–174° cor. (6), 166–168° (8). {From Č with Br_2 (6).}

3:7600 (1) Silva, *Ber.* **7**, 953 (1874); *Ber.* **6**, 36 (1873). (2) Aschan, *Ber.* **31**, 1802 (1898). (3) Pavlov, *Ann.* **196**, 124 (1879). (4) Henry, *Rec. trav. chim.* **25**, 147 (1906). (5) Whitmore, Rothrock, *J. Am. Chem. Soc.* **55**, 1107–1108 (1933). (6) Bartlett, Condon, Schneider, *J. Am. Chem. Soc.* **66**, 1533, 1537 (1944). (7) Whitmore, Laughlin, *J. Am. Chem. Soc.* **55**, 3735 (1935) (8) Grosse, Ipatieff, *J. Org. Chem.* **8**, 440–441 (1943).

3:7603 *d,l*-α-METHYL-*n*-BUTYRYL CHLORIDE C_5H_9OCl Beil. II - 306
(Ethyl-methyl-acetyl chloride) II₁—
II₂-(270)



B.P. 118.0–118.3° at 761 mm. (1) $D_4^{20} = 0.9917$ (1) $n_D^{20} = 1.41695$ (1)
115.8–116.6° (2)
115–116° (3)

{The dextrorotatory form of Č, b.p. 119–120°, $D_4^{24} = 0.990$, $n_D^{17.5} = 1.4177$, has also been reported (4).}

{For prepn. of Č from *d,l*-2-methylbutanoic acid-1 (1:1105) with $SOCl_2$ see (1).}

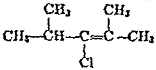
{For actn. of PCl_5 on Č see (5).}

Č with K ethyl-methyl-acetate *yields* (6) corresp. anhydride, b.p. 103–104° at 17 mm.

Č on hydrolysis yields *d,l*-ethyl-methyl-acetic acid (1:1105) (for the amide, anilide, *p*-toluidide, and other derivs. corresp. to Č see 1:1105).

3:7603 (1) Leimu, *Ber.* **70**, 1049 (1937). (2) Kohlrausch, Pongratz, *Z. physik. Chem.* **B-22**, 382 (1933). (3) Rupe, *Ann.* **369**, 335 (1909). (4) Kenyon, Phillips, Pittman, *J. Chem. Soc.* **1935**, 1080. (5) von Braun, Jostes, Münch, *Ann.* **453**, 146–147 (1927). (6) Verkade, *Rec. trav. chim.* **36**, 203 (1916).

3:7605 3-CHLORO-2,4-DIMETHYLPENTENE-2 $C_7H_{13}Cl$ Beil. I - 221
I₁—
I₂—



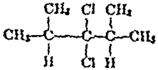
B.P. 118–120° (1) $D_4^{0} = 0.9513$ (1)

{For prepn. of Č from 2,4-dimethylpentanone-3 (di-isopropyl ketone) (isobutyrone) (1:5433) with PCl_5 see (1).}

Č with alc. KOH gives (1) 2,4-dimethylpentadiene-2,3 (tetramethylallene) {Beil. I-258, I₁-(121)}, b.p. 70° (1), 86.5° at 763 mm. {Beil. I₁-(121)}.

3:7605 (1) Henry, *Ber.* **8**, 400 (1875).

3:7610 3,3-DICHLORO-2,4-DIMETHYLPENTANE $C_7H_{14}Cl_2$ Beil. I - 158
I₁—
I₂—



B.P. 118–120° sl. dec. (1) $D_{-}^{0} = 0.9513$ (1)

3:7625 α-CHLOROETHYL ACETATE $C_4H_7O_2Cl$ Beil. II - 152, II_1-(71), II_2—

$$CH_3.\overset{H}{\underset{Cl}{C}}.O.CO.CH_3$$

B.P. 121.5° at 746 mm. (sl. dec.)	(1)	$D^{15}_{15} = 1.114$ (1)
119–120° at 740 mm.	(2)	
119–121° at 740 mm.	(3)	
113–116° at 740 mm.	(3) (4)	

Note that the same observers have noted (3) two dif. b.p.'s, viz., 119–121° and 113–116° both at 740 mm., on dif. prepns.; this anomaly is still unexplained.

[For prepn. of C̄ (75% yield (5)) from paraldehyde (1:0170) + AcCl (3:7065) + trace $ZnCl_2$ see (5) (1); from acetaldehyde (1:0100) + AcCl (3:7065) at 100° see (6); from vinyl acetate + liq. (3) or gas (7) HCl see (3) (7).]

C̄ on htg. with 0.02% $ZnCl_2$ at 80° yields acetaldehyde (1:0100) + AcCl (3:7065) + paraldehyde (1:0170) (8); C̄ passed through a tube at 360–380° or over pumice at 250–300° yields acetaldehyde + acetyl chloride (9).

C̄ with aq. slowly hydrolyzes in cold, more rapidly on warming, yielding acetaldehyde (1:0100), AcOH (1:1010), and HCl. [This hydrolysis is accelerated by trace of acid, e.g., $N/10$ HCl (10).]

3:7625 (1) Franchimont, *Rec. trav. chim.* **1**, 245–246 (1882). (2) Descudé, *Compt. rend.* **132**, 1568 (1901). (3) Gebauer-Fuelnegg, Moffett, *J. Am. Chem. Soc.* **56**, 2009 (1934). (4) Ulich, Adams, *J. Am. Chem. Soc* **43**, 663 (1921). (5) Colonge, Mostafavi, *Bull. soc. chim.* (5) **5**, 1485–1486 (1938). (6) Simpson, *Ann* **109**, 156–157 (1859). (7) Ger. 313,696, July 19, 1919; *Cent.* **1919**, IV 664. (8) Brit. 329,721, June 17, 1930; *Cent.* **1930**, II 1611. (9) Brit. 330,511, July 10, 1930; *Cent* **1930**, II 2184 (10) Drushel, Bancroft, *Am. J. Sci.* (4) **44**, 376 (1917).

3:7630 1-CHLOROHEXENE-1 $C_6H_{11}Cl$ Beil. S.N. 11

$$CH_3.CH_2.CH_2.CH_2—CH{=}\overset{Cl}{CH}$$

B.P. 121–121.5° (1) $D^{22}_{-} = 0.8872$ (1) $n^{22}_{D} = 1.4300$ (1)

[For formn. of C̄ (together with other prods.) from either 3,3-dichloropropene-1 (3:5140) or 1,3-dichloropropene-1 (3:5280) with n-propyl MgBr see (1).]

C̄ does not react with NaOEt at 130° (1).

C̄ readily reacts with Na yielding (1) hexene-1 (1:8255), b.p. 64°.

C̄ adds Br_2 yielding (1) 1,2-dibromo-1-chlorohexane, b.p. 107° at 13 mm., $D^{24}_{-} = 1.664$, $n^{24}_{D} = 1.515$ (1).

3:7630 (1) Kirrmann, Grard, *Compt. rend.* **190**, 876–877 (1930); *Bull. soc. chim.* (4) **47**, 843–847 (1930).

3:7640 4-CHLOROBUTANONE-2 C_4H_7OCl Beil. I - 670, I_1—, I_2-(731)

(β-Chloroethyl methyl ketone; 1-chlorobutanone-3)

$$CH_3—\underset{\overset{\|}{O}}{C}—CH_2—\underset{Cl}{CH_2}$$

B.P. 120–122°	at 760 mm.	(1)
50–55°	at 16 mm.	(2)
53–55°	at 16 mm.	(8)
53°	at 15 mm.	(7)
50°	at 15 mm.	(3)
48–50°	at 15 mm.	(4)

[*See also 3-chlorobutanone-2* (3:7598).]

Liquid with faint and not disagreeable odor.

[For prepn. of $\bar{C}$ from methyl vinyl ketone [Beil. I-728, I_1-(379), I_2-(786)] satd. at 0° with HCl gas directly (67% yield (4)) or in C_6H_6 soln. (5); from acetyl chloride (3:7065) with ethylene + $AlCl_3$ at 0° (yields: 33% (3), 53% (6)) cf. (2) or at 100° and 50 atm. press. (22); from 4-chlorobutadiene-1,2 (3:7225) by cat. hydration with conc. H_2SO_4 at −5° (yield 54% crude $\bar{C}$ (1)); from β-chloropropionyl chloride (3:5690) with $Zn(CH_3)_2$ (60% yield (7)); from butanol-1-one-3 (γ-keto-*n*-butyl alcohol) by saturation with HCl gas at 0° espec. in pres. of 5–10% $AlCl_3$ (63% yield (8)) see indic. refs.] — [Note that $\bar{C}$ is *not* formed by chlorination of ethyl methyl ketone (butanone-2) (21).]

$\bar{C}$ with hot aq. alk. or alk. carbonates gives only resins, but $\bar{C}$ on boilg. with dimethylaniline or better diethylaniline loses HCl giving (yields: 30% and 80%, respectively (7)) methyl vinyl ketone (see above), b.p. 79–80°; note, however, that $\bar{C}$ on warming with alc. KOH or quinoline loses both HCl and H_2O yielding (4) a mixt. of dienes, b.p. 65–75°.

[For behavior of potential $\bar{C}$ (mixt. of methyl vinyl ketone + HCl gas in C_6H_6) with ethylene glycol (1:6465) see (5); for reactn. of $\bar{C}$ with trimethylene glycol (1:6490) + K yielding γ-hydroxypropyl γ-keto-*n*-butyl ether see (3).]

[$\bar{C}$ with β-naphthol (1:1540) in EtOH/KOEt at 0° for 3 days gives (59% yield (9)) 1-(γ-keto-*n*-butyl)naphthol-2, cryst. from aq. alc., m.p. 88–89° (corresp. semicarbazone, pale yel. pr. from MeOH, m.p. 179–180° (9)).]

[$\bar{C}$ with 2-methylcyclohexanone (1.5470) in EtOH/NaOEt (or sodium isopropylate/isopropyl alc.) at 0° for 18 hrs. gives (yields: 15% (10), 10% (20)) 2-keto-10-methyl-2,3,4,5,6,7,8,10-octahydronaphthalene, b.p. 129–133° at 12 mm., n_D^{12} = 1.5250 (10).]

[$\bar{C}$ with diethyl sodio-methylmalonate in ether gives (11) diethyl (methyl)-(γ-keto-*n*-butyl)malonate, b.p. 114–116° at 0.4 mm.; $\bar{C}$ with ethyl α-isopropylacetoacetate in EtOH/NaOEt as directed yields (13) ethyl Δ-(1)*p*-menthenone-3-carboxylate-4.]

[$\bar{C}$ with aniline + conc. HCl or 40% H_2SO_4 htd. with nitrobenzene or H_3AsO_4 yields (14) (6) lepidine (4-methylquinoline) [Beil. XX-395, XXI_1-(150)]; for corresp. reactn. with other amines see (14) (6).]

[$\bar{C}$ with 1-aminoanthraquinone [Beil. XIV-177, XIV_1-(436)] in pyridine yields (15) 1-(γ-keto-*n*-butylamino)anthraquinone, dark red cryst. which dye cellulose acetate.]

[$\bar{C}$ with hydrazine hydrate in MeOH gives (80% yield (16)) (17) (19) by ring closure 3-methyl-Δ^2-pyrazoline [Beil. XXIII-30], liq., b.p. 56° at 15 mm. (16), sol. aq. but forming the corresp. picrate, B̄.PkOH, yel. ndls. from alc., m.p. 153° (16) (17) (19). — $\bar{C}$ in AcOH with methylhydrazine sulfate + NaOAc in aq. stood 2 hrs. gives (18) 1,3-dimethyl-Δ^2-pyrazoline, oil, which with ethereal picric acid gives the corresp. picrate, B̄.PkOH, m.p. 131.5–132.5° (18). — $\bar{C}$ with phenylhydrazine in ether gives (16) by ring closure 3-methyl-1-phenyl-Δ^2-pyrazoline, ndls. from ether by addn. of pet. ether, m.p. 76–77° (16).]

[$\bar{C}$ with $NH_2OH.HCl$ + K_2CO_3 in aq. MeOH htd. for a few minutes gives (20% yield (16)) by ring closure 3-methyl-Δ^2-isoxazoline [Beil. XXVII-12], oil, b.p. 60° at 15 mm. (16).]

Ⓓ **1-Carbamido-3-methyl-Δ^2-pyrazoline:** ndls. from EtOAc, m.p. 167–168° (18), 167° (16). [Note that $\bar{C}$ with 1 equiv. semicarbazide HCl + NaOAc in aq. immediately ppts. the corresp. semicarbazone; this on htg. for 10 min. with strong aq. NaOAc (or $\bar{C}$ + semicarbazide HCl + strong NaOAc soln. htd. directly in dil. alc. (19)) loses HCl and ring-closes to the indicated deriv.]

Ⓓ **1-Phenyl-3-methyl-Δ^2-pyrazoline:** ndls. from ether on addn. of pet. eth., m.p. 76–77° (16), 77° (1). [From $\bar{C}$ in ether with phenylhydrazine, followed by neutralization and drying with anhyd. K_2CO_3 (16) (1); note that the presumably intermediate phenylhydrazone loses HCl and by ring closure gives the indicated deriv.]

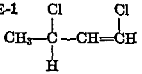
3:7640 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* **54**, 4070 (1932). (2) Schoeller, Zöllner (to Schering-Kahlbaum, A.G.), U.S. 1,737,203, Nov. 26, 1929, *Cent.* **1930**, II 1133; Brit.

282,412, Feb. 15, 1928; *Cent.* **1929,** I 143. (3) McGinnis, Robinson, *J. Chem. Soc.* **1941,** 405–406. (4) Smith, Sprung, *J. Am. Chem. Soc.* **65,** 1279–1280 (1932). (5) Kühn, *J. prakt. Chem.* (2) **156,** 125 (1940). (6) Kenner, Statham, *Ber.* **69,** 17 (1936). (7) Blaise, Maire, *Bull. soc. chim.* (4) **3,** 268–270 (1908). (8) Décombe, *Compt rend* **202,** 1685–1687 (1936). (9) McQuillin, Robinson, *J. Chem. Soc.* **1941,** 588–589. (10) du Feu, McQuillin, Robinson, *J. Chem. Soc.* **1937,** 53, 58–59.

(11) Lin, Robinson, *J. Chem. Soc.* **1938,** 2006. (12) This reference deleted. (13) Walker, *J. Chem. Soc.* **1935,** 1585. (14) Schering-Kahlbaum, A.G., Brit. 283,577, March 7, 1928; *Cent.* **1929,** I 3148. (15) I.G., Brit. 485,175, June 9, 1938; French 828,581, May 20, 1938; *Cent.* **1938,** II 3465. (16) Maire, *Bull. soc. chim.* (4) **3,** 274–279 (1908). (17) Freudenberg, Stoll, *Ann.* **440,** 44 (1924). (18) von Auwers, Heimke, *Ann.* **458,** 205 (1927). (19) von Auwers, Ludewig, *Ber.* **69,** 2348–2349 (1936). (20) Décombe, *Compt. rend.* **213,** 579–581 (1941); *Cent.* **1942,** II 1568.

(21) Forster, Fierz, *J. Chem. Soc.* **93,** 669 (1908). (22) Frolich, Wiezevich (to Standard Oil Development Co.), U.S. 2,006,198, June 25, 1935; *Cent.* **1936,** I 2827; *C.A.* **29,** 5457 (1935).

3:7650 1,3-DICHLOROBUTENE-1 $C_4H_6Cl_2$ **Beil. S.N. 11**



B.P. 120–123° (1) D_{20}^{20} **= 1.130 (1)** n_D^{20} **= 1.464 (1)**

Note. $\bar{C}$ by virtue of facile allylic transposition easily isomerizes to 1,1-dichlorobutene-2 (3:7685) q.v.

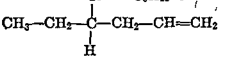
[For prepn. of $\bar{C}$ from crotonaldehyde (1:0150) with PCl_5 see (1) (2); the resulting mixt. of $\bar{C}$ with its synionic isomer (1,1-dichlorobutene-2) (supposed by (2) to have been only the latter) has been separated by very precise fractnl. distn. (1).]

$\bar{C}$ with NaOEt yields (1) 1-chloro-3-ethoxybutene-1, b.p. 132–133° at 760 mm., 54–55° at 46 mm., $D_{16}^{16} = 0.960$, $n_D^{16} = 1.432$ (1).

$\bar{C}$ with NaOAc yields (1) 1-chloro-3-acetoxybutene-1, b.p. 57–58° at 16 mm., $D_{17}^{17} = 1.090$, $n_D^{17} = 1.443$ (1). [Note that crotylidene diacetate (1,1-diacetoxybutene-2), prepd. (95% yield (3)) from crotonaldehyde (1:1050) with Ac_2O, gives (3) with dry HCl the isomeric 3-chloro-1-acetoxybutene-1, b.p. 64° at 13 mm., $D_{20}^{20} = 1.083$, $n_-^{20} = 1.451$ (3).]

3:7650 (1) Kirrmann, *Compt. rend.* **199,** 1228–1229 (1934). (2) Kekulé, *Ann.* **162,** 98–100 (1872). (3) Kirrmann, *Bull. soc. chim.* (5) **5,** 917–918 (1938).

3:7655 *d,l*-4-CHLOROHEXENE-1 $C_6H_{11}Cl$ **Beil. I - 215**
(Allyl-ethyl-carbinyl chloride) I_1— I_2—



B.P. 120–123° dec. (1)

[For prepn. of $\bar{C}$ from hexen-1-ol-4 (allyl-ethyl-carbinol) [Beil. I-444] with PCl_5 see (1).]
$\bar{C}$ with alc. KOH yields (1) hexadiene-1,3 [Beil. I-253], b.p. 72–74°.

3:7655 (1) Fournier, *Bull. soc. chim.* (3) **15,** 402, 886 (1896).

(11) Grimaux, Adam, *Bull. soc. chim.* (2) **36**, 19–21 (1881). (12) Barbaglia, *Ber.* **7**, 467–469 (1874). (13) Consortium für Elektrochem. Ind., French 707,852, July 16, 1931; *Cent.* **1931**, II 2056. (14) Akashi, *Bull. Inst. Phys.-Chem. Research* (*Tokyo*) **12**, 329–340 (1933); *Cent.* **1933**, I 3066; *C.A.* **27**, 3447 (1933). (15) Kling, *Bull. soc. chim.* (3) **33**, 322–323 (1905); *Ann chim.* (8) **5**, 474–475 (1905). (16) Fritsch, *Ber.* **26**, 598 (1893); *Ann.* **279**, 315–316 (1894). (17) Malinovskii, *J. Gen. Chem.* (*U S S R.*) **9**, 832–839 (1939), *C.A.* **34**, 375 (1940). (18) Erlenbach, *Ann.* **269**, 18–19 (1892). (19) Wislicenus, *Ber* **43**, 3532–3533 (1910). (20) Smirnoff, *J. Russ. Phys.-Chem. Soc.* **35**, 854–872 (1903); *Cent* **1904**, I 576

(21) Henry, *Compt. rend.* **94**, 1428 (1882). (22) Völker, *Ann.* **192**, 93–95 (1878). (23) von Romburgh, *Verslag Akad Wetenschappen Amsterdam* **31**, 655–656 (1922), *Cent.* **1924**, I 159; *C.A.* **18**, 1271 (1924). (24) Ingold, *J. Chem. Soc.* **119**, 328–329 (1921). (25) Ingold, Sako, Thorpe, *J Chem. Soc* **121**, 1197 (1922). (26) Dem'yanov, Feofilaktov, *J. Gen. Chem.* (*U.S S.R.*) **9**, 340–360 (1939), *Cent.* **1939**, II 2913; *C A* **34**, 385 (1940). (27) Winkel, Proske, *Ber.* **69**, 700–701 (1936). (28) Klimont, *Chem. Ztg.* **69**, 521 (1922). (29) Hess, Fink, *Ber.* **48**, 2004 (1915). (30) Raschig, Prahl, *Ber* **59**, 2027–2028 (1926)

(31) Prjanischnikow, Leontowitsch, *Ber.* **68**, 1867 (1935). (32) Kuhn, *J. prakt. Chem.* (2) **156**, 121 (1940) (33) Rojahn, Lemme, *Arch. Pharm.* **263**, 615–616 (1925). (34) Fromm, Kapeller, Taubmann, *Ber.* **61**, 1357–1358 (1928). (35) Glattfeld, Schneider, *J. Am. Chem. Soc.* **60**, 417 (1938). (36) Fourneau, *Bull. soc. chim* (4) **29**, 413–414 (1921). (37) I.G., French 785,705, Aug. 17, 1935, *Cent.* **1936**, I 1134. (38) Hooper, Johnson, *J Am. Chem. Soc* **56**, 470–471 (1934). (39) Johnson (to Winthrop Chem. Co.), U.S 2,014,493, Sept. 17, 1935; *Cent.* **1936**, I 1114, *C.A.* **29**, 7344 (1935). (40) Suter, Johnson, *Rec trav. chim* **49**, 1066–1068 (1930).

(41) Huntress, Pfister, *J. Am. Chem. Soc.* **65**, 1668–1670 (1943). (42) Wheeler, *J. Am. Chem. Soc.* **51**, 3654 (1929). (43) Allen, Gates, *J Am. Chem. Soc.* **6**, 596–601 (1941).

3:0565 PHENYL CHLOROACETATE $C_8H_7O_2Cl$ Beil. **VI - 153**, **VI$_1$-(87)**, **VI$_2$-(154)**

$ClCH_2.CO.O$— 

M.P.		B.P.				
45°	(1) (2)	**230–235°**		(6)	D_4^{44} = **1.2202** (9)	n_D^{44} = **1.5146** (9)
44–45°	(3)	**155°**	at 65 mm.	(7)		
44°	(5)	**123–126°**	at 14 mm.	(2)		
43°	(7)					
40.2°	(6)					

Ndls. or lfts. from alc. — Insol. aq.; eas. sol. alc., ether.

[For prepn. of C̄ from phenol (1:1420) with chloroacetyl chloride (3 5235) on htg. alone (7) (6) (3), in ether soln. + pyridine (2), or with $AlCl_3$ in CS_2 (1) see indic refs.; with chloroacetic acid (3·1370) + P_2O_5 in $CHCl_3$ (8) or on htg. with $POCl_3$ or $ZnCl_2$ (5) see (8) (5).]

C̄ hydrolyzes rather easily, even slowly on stdg. in moist air (3) C̄ on mere refluxing for ¾ hr. with abs. alc. or with alc. NaOEt undergoes trans-esterification yielding (3) ethyl chloroacetate (3:5700) and phenol (1:1420)

C̄ in ether treated with NH_3 gas reacts vigorously yielding (3) NH_4 phenolate (sol. in aq.) and chloroacetamide (insol. aq), m p. **118°** (3).

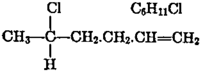
C̄ with aniline (2 moles) at 80° for 1 hr gives (4) aniline hydrochloride (sol. in aq.) + phenyl *N*-phenylaminoacetate [Beil. XII-471] *pptd from alc. by addn of aq , m p* 82–83° (4). [Note that C̄ on boilg with aniline yields (4) *N*-phenylaminoacetanilide (*N*-phenylglycine anilide) [Beil. XII-556], m p. 111–112° (4)]

C̄ with phenylhydrazine (2 moles) at 50° for ¼ hr. yields (4) phenyl β-phenylhydrazinoacetate [Beil XV-321], lfts. from C_6H_6 or from alc. by addn. of aq., m p. 93–94° (4).

C̄ htd. with $AlCl_3$ for 5 hrs. at 130–140° gives (10) *o*-hydroxyphenacyl chloride (vol. with steam), m p. 74°, + *p*-hydroxyphenacyl chloride (not vol. with steam), m.p 148°.

C̄ + equal wt. pyridine htd. at 100° gives (1) cpd. $\bar{C}.C_5H_5N.5H_2O$, ndls. from alc., m p. 165–168° dec. (11), cf. (4).

3:7665. *d,l*-5-CHLOROHEXENE-1 $C_6H_{11}Cl$ Beil. I - 215
(Biallyl hydrochloride) I_1—
I_2-(192)



B.P. 121–125° at 760 mm. (1)	D_4^{25} = 0.8891 (1)	n_D^{25} = 1.4279 (1)
120–124° (2)		
64–66° at 103 mm. (1)	D_4^{20} = 0.9141 (1)	n_D^{20} = 1.4305 (1)
43–45° at 45 mm. (1)		n_D^{15} = 1.4332 (1)
28–30° at 13 mm. (1)	D_4^{12} = 0.9105 (2)	n_D^{12} = 1.4350 (2)

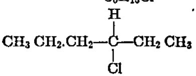
[The levorotatory isomeride of $\bar{C}$ has also been reported (3) from dextrorotatory hexen-1-ol-5 with PCl_5 in ether, b.p. 119–122° (3); ozonolysis followed by treatment with Br_2/aq. yields (3) levorotatory γ-chloro-*n*-valeric acid.]

[For prepn. of $\bar{C}$ from hexadiene-1,5 (biallyl) (1:8045) by shaking at room temp. with 5 vols. conc. HCl for 120 hrs. see (1) (4) (yield of $\bar{C}$ is 23% accompanied by 57% 1,5-dichlorohexane (3:9340) and other products (1)); for prepn. of $\bar{C}$ from hexen-1-ol-5 [Beil. I-444] with PCl_5 in $CHCl_3$ (30% yield + much resin (2)) see (2) (attempts to obt. $\bar{C}$ from this alc. with HCl gave (2) as a result of ring closure only 2,5-dimethyltetrahydrofuran [Beil. XVII-14], b.p. 93°).]

$\bar{C}$ on oxidn. with CrO_3/H_2SO_4 for 2½ hrs. at 90–95° gave (2) formic acid (1:1005) but no allylacetone.

3:7665 (1) Cortese, *J. Am. Chem. Soc.* **52**, 1519–1521 (1930). (2) Courtot, Pierron, *Compt. rend.* **190**, 1057–1059 (1930). (3) Levene, Haller, *J. Biol. Chem.* **83**, 599 (1929). (4) Wurtz, *Ann. chim.* (4) **3**, 171 (1864).

3:7670 3-CHLOROHEXANE $C_6H_{13}Cl$ Beil. S.N. 10
(*sec.*-(3)-Hexyl chloride;
ethyl-*n*-propyl-carbinyl chloride)



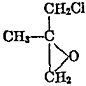
B.P. 123° (1)	D_{20}^{20} = 0.870 (2)	n_D^{20} = 1.4163 (2)
59.5–60° at 95 mm. (2)		

[For prepn. of $\bar{C}$ from hexene-3 (1:8270) in $CHCl_3$ by shaking with conc. HCl for 48 hrs. (45% yield) (HCl gas in $CHCl_3$ fails) see (2) (for study of rate of reaction in various solvents see (4)); from hexanol-3 (1:6203) in ether + HCl gas for 5 days see (1); for formn. of $\bar{C}$ (together with other products) from reactn of 2-ethylbutanol-1 (1:6223) with HCl + $ZnCl_2$ see (3).]

$\bar{C}$ with Mg in dry ether gives RMgCl which with O_2 yields (3) hexanol-3 (1:6203); this alc. upon oxidn. with CrO_3/H_2SO_4 yields (3) hexanone-3 (2,4-dinitrophenylhydrazone, m.p. 146.5–148.5° (3); semicarbazone, m.p. 110.5–111.5° (3)).

3:7670 (1) Lagerev, Shadmanov, *Trudy Uzbekskego Gosudarst. Univ.* **6**, 89–91 (1936); *C.A.* **35**, 2120 (1941). (2) Spiegler, Tinker, *J. Am. Chem. Soc.* **61**, 942 (1939). (3) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2535 (1938). (4) O'Connor, Baldinger, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1455 (1939).

3:7657 3-CHLORO-2-METHYL-1,2-EPOXYPROPANE C_4H_7OCl Beil. S.N. 2362
(" β-Methylepichlorohydrin ")



B.P. 122.0° (1) **D_4^{20} = 1.1025 (1)** **n_D^{20} = 1.4340 (1)**

Colorless liq.; C̄ is sol. aq. to extent of 3 g. in 100 g. aq. at 20° (1). — C̄ with aq. forms a const.-boilg. mixt. (b.p. 89.8°) contg. 74.4% C̄ + 25.6% aq. (1).

[For prepn. of C̄ from 1,3-dichloropropanol-2 (dichloro-*ter*-butyl alcohol) (3:5985) with aq. $Ca(OH)_2$ (93% yield (1)) see (1) (2); from chloroacetone (3:5425) with diazomethane in ether see (3).]

C̄ with aq. especially at elevated temps., or C̄ stirred for 3 hrs. at 90–95° with aq. contg. 0.1% H_2SO_4 until mixt. becomes homogeneous, gives (1) (4) (by hydration through ring opening) 95% yield (1) 3-chloro-2-methylpropanediol-1,2 (β-methylglycerol monochlorohydrin) (3:9190). [Note that alk. also catalyzes this hydration but reacts with the prod.] [Note also that HCl may not be used since it adds to the epoxy ring yielding (3) 1,3-dichloro-2-methylpropanol-2 (3:5977).]

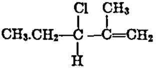
C̄ on distn. with 12% H_2SO_4 at ord. press. yields (1) (5) quant. α-methylacrolein (" methacrolein ") [Beil. I-731].

C̄ with conc. aq. NH_4OH + alk. yields (1) 1,3-diamino-2-methylpropanol-2 [Beil. IV_2-(739)].

3:7657 (1) Hearne, DeJong, *Ind. Eng. Chem* **33**, 940–943 (1941). (2) Groll, Hearne (to Shell

(1938).

3:7660 *d,l*-3-CHLORO-2-METHYLPENTENE-1 $C_6H_{11}Cl$ Beil. S.N. 11
(α-Ethyl-β-methylallyl chloride)



B.P. 120–124° (1)

Note. C̄ by virtue of allylic transposition would be expected to be in equilibrium with its synionic isomer 1-chloro-2-methylpentene-2 (γ-ethyl-β-methylallyl chloride). The material reported by (1) was regarded as C̄; the isomer appears to be as yet unrecorded.

[For prepn. of C̄ from 2-methylpenten-1-ol-3 by htg. with $SOCl_2$ + pyridine at 65° for 4 hrs. see (1).]

C̄ in MeOH refluxed 4 hrs. with NaSCN gives (1) α-ethyl-β-methylallyl isothiocyanate, b.p. 100–200° at 760 mm., 75–90° at 10 mm. (1). [This prod. with conc. H_2SO_4 at 0° yields 4-ethyl-5,5-dimethyl-2-mercaptothiazoline, color cryst. from alc., m.p. 115–118° (1).]

3:7660 (1) Bruson, Eastes, *J. Am. Chem. Soc.* **59**, 2013 (1937).

Colorless liq. with not disagreeable odor.

[For prepn. of C̄ from butene-1 with Cl_2 in aq. (5), in CCl_4 (2), or at elevated temp. and press. in pres. of $CaCl_2$ + other cat. (8) (some 1,2,3-trichlorobutane (3:5935) is also formed (5)) see indic. refs.; for prepn. of C̄ from 1-chlorobutane (3:7160) with Cl_2 in sunlight or u.v. light (other isomers are also formed) see (9) (10) (11) (4) (7) (other isomers are always formed, and yield of C̄ is about 17% (7)) see indic. refs.; for formn. of C̄ from 2-chlorobutane (3:7125) with Cl_2 in light see (6).]

[C̄ with Cl_2 at −17° in dark gives (12) 1,2,3-trichlorobutane (3:5935) as main product.]

[C̄ is not hydrolyzed by boilg. aq. K_2CO_3 (6) but on htg. with excess 7–15% aq. $NaHCO_3$ + Na_2CO_3 at 135–195° under press. for 1–6 hrs. gives (13) butanediol-1,2 [Beil. I-477, I_2-(545)] + 2-chlorobutene-2 (3:7105) + ethyl methyl ketone (1:5405) + mixt. of buten-1-ol-3 and buten-2-ol-1.]

[C̄ passed as vapor over heated soda-lime as directed (9) (4) (10) (11), or C̄ + aq. vapor at 200–500° over silica gel + cat. (14), gives (24.8% yield (9)) butadiene-1,3 (divinyl) [Beil. I-249, I_1-(107), I_2-(224)].]

[C̄ with alc. KOH (1 mole + 25% excess) refluxed 3 days gives a mixt. contg. (2) cf. (18) 2-chlorobutene-1 (3:7075) + *cis*-1-chlorobutene-1 (3:7110) + *trans*-1-chlorobutene-1 (3:7110); note that by this method no butyne-1 is formed (15) and can be obtd. from C̄ + alc. KOH only by very drastic treatment, e.g., htg. in s.t. at 130–135° for 16–20 hrs. (15).]

[For reactn. of C̄ with phenylacetonitrile (benzyl cyanide) + $NaNH_2$ in liq. NH_3 giving (40% yield (16)) 1-cyano-2-ethyl-1-phenylcyclopropane, b.p. 93–94° at 1 mm., D_4^{20} = 0.9921, n_D^{20} = 1.52457, see (16); for condens. of C̄ with diphenyl ether (1:7125) + $AlCl_3$ see (17).]

3:7680 (1) [illegible] 36, 504 (1927). (2) Navez, *Bull. soc. chim. Belg.* 39, 435–440 [illegible] *ysik. Chem.* B-48, 9 (1940). (4) Perkin, [illegible]
(17) Coleman, Hadler (to Dow Chem. Co.), [illegible]
(18) Henne, Hinkamp, *J. Am. Chem. Soc.* 67, 1197 (1945).

3:7685 1,1-DICHLOROBUTENE-2 $C_4H_6Cl_2$ Beil. I - 205
(Crotylidene (di)chloride) $CH_3—CH{=}CH—CHCl_2$ I_1— I_2—

B.P. 124–125° (1) D_{18}^{18} = **1.140 (1)** n_D^{18} = **1.466 (1)**

C̄ by virtue of facile allylic transposition easily isomerizes to 1,3-dichlorobutene-1 (3:7650) q.v.

[For prepn. of C̄ from crotonaldehyde (1:0150) with PCl_5 see (1) (2); the resulting mixt. of C̄ with its synionic isomer (1,3-dichlorobutene-1) (supposed by (2) to have been only C̄) has been separated by very precise fractional distn. (1).]

3:7675 *d,l*-4-CHLOROHEXENE-2 $C_6H_{11}Cl$ Beil. I - 215
(α-Ethyl-γ-methylallyl chloride; α-ethylcrotyl chloride) I_1— I_2-(192)

$CH_3CH_2—C(Cl)(H)—CH{=}CH.CH_3$

B.P.				
123–124° at 760 mm., sl. dec.	(1)		$n_D^{25} = 1.4356$	(4)
122–126° dec.	(2) (3)	$D_{20}^{20} = 0.9148$ (6)		
73–76° at 136 mm.	(4)		$n_D^{20} = 1.4400$	(1)
66–67° at 110 mm.	(5)		1.4385	(5)
65–67° at 110 mm.	(2)		1.4382	(5)
65–70° at 110 mm.	(3)			
38–43° at 30 mm.	(6)			
30° at 13 mm.	(1)			
30° at 10 mm.	(7)			

Note. The possibility that C̄ may by virtue of allylic transposition exist or react in the form of its as yet unisolated synionic isomer 2-chlorohexene-3 (γ-ethyl-α-methylallyl chloride) should not be overlooked.

[For prepn. of C̄ from hexen-2-ol-4 (α-ethyl-γ-methylallyl alcohol) (1) [Beil. I-445] with dry HCl gas at 0° (5) (81% yield (2)), with conc. aq HCl (7), with PCl_5 (5) (6) (54% yield (8)), or with $SOCl_2$ in ether + quinoline at 0° (1) see indic. refs.]

C̄ is readily hydrolyzed. C̄ on shaking with aq. at 15° is 81% hydrolyzed in 48 hrs.; 100% in 90 min. at 40° (2). — C̄ with 2½ pts. aq. + 1 pt. $CaCO_3$ stood 3 days gives in good yield (1) 4-chlorohexen-2-ol, b.p. 49–50° at 12 mm. (1) [acid phthalate, m.p. 52–53° (1); p-nitrobenzoate, m.p. 35–37° (1); N-(p-xenyl)carbamate, m.p. 102° (1)].

C̄ on htg. in s.t. at 120° with MeOH/KOH gives (3) 4-methoxyhexene-2, b.p. 110–113° (3).

[For reactn. of C̄ with phenol + K_2CO_3 in acetone see (8) (5); for extension to many phenols see (6); for reactn. of C̄ with diethylsodiomalonate see (4); for reactn. of C̄ with NH_3 or amines see (9).]

C̄ on oxidn. with CrO_3/H_2SO_4 at 40° gives (55% yield (2)) hexen-2-one-4, b.p. 137–140° (2) [2,4-dinitrophenylhydrazone, m.p. 100–101° (2)].

3:7675 (1) Airs, Balfe, Kenyon, *J. Chem. Soc.* **1942**, 24–26. (2) Courtot, Pierron, *Bull. soc. chim.* (4) **45**, 290–291 (1929). (3) Reif, *Ber.* **39**, 1603–1604 (1906), **41**, 2742 (1908). (4) Shonle, Waldo, *J. Am. Chem. Soc.* **55**, 4649–4652 (1933). (5) Smith, Ungnade, Lauer, Leekley, *J. Am. Chem. Soc.* **61**, 3080 (1939). (6) Hurd, Puterbaugh, *J. Org. Chem.* **2**, 381–386 (1937). (7) Boettcher (to I.G.), Ger. 513,364, Nov. 26, 1930; *Cent.* **1931**, I 1007, *C.A.* **25**, 1260 (1931). (8) Hurd, Cohen, *J. Am. Chem. Soc.* **53**, 1917–1922 (1931). (9) Boettcher (to I.G.), Ger. 487,787, Dec. 16, 1929, *Cent.* **1930**, I 1050.

3:7680 *d,l*-1,2-DICHLOROBUTANE $C_4H_8Cl_2$ Beil. I —
(α-Butylene dichloride) I_1-(38) I_2-(81)

$CH_3—CH_2—CH(Cl)—CH_2Cl$

B.P.				
121.0°	(1) (2) (6)	$D_4^{25} = 1.1116$ (2)		
123–126° at 760 mm.	(3)		$n_D^{20} = 1.440$	(7)
abt. 125°	(4)	$D_4^{20} = 1.1182$ (6)		
123–125° at 758 mm.	(7)	1.1187 (7)		
121–122° at 735 mm.	(5)	$D_4^{15} = 1.1244$ (2)	$n_D^{15} = 1.4474$	(2)
31° at 28 mm.	(5)		1.4472	(3)

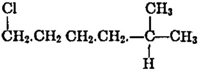
hydrazine, m.p. 108° (1)), and β-phenyl-n-butyrophenone (1,3-diphenylbutanone-1) [Beil. VII-453], m.p. 74° (1) (11). — For reactn. of C̄ with $AlCl_3$ + p-xylene (16), mesitylene (11), acenaphthene (17), anisole (18), methyl p-tolyl ether (7), methyl 3,5-dimethylphenyl ether (19) see indic. refs.]

C̄ on hydrolysis with aq. yields α-crotonic acid (1:0425), m.p. 72°; for the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see 1:0425.

3:7693 (1) Kohler, *Am. Chem. J.* **42**, 395–396 (1909). (2) Staudinger, Becker, Hirzel, *Ber.* **49**, 1991 (1916). (3) Luniak, *Ber.* **42**, 915–916 (1909) (4) Henry, *Bull. acad. roy. Belg.* (3) **36**, 42 (1898); *Cent.* **1898**, II 663. (5) Maxim, *Bul. Soc. Chim. România*, **10**, 97–115 (1928); *Cent.* **1929**, I 2161; *C.A.* **23**, 2697 (1929). (6) Jones, Mason, *J. Am. Chem. Soc.* **49**, 2533 (1927). (7) von Auwers, *Ann.* **421**, 30–36 (1921). (8) Kohlrausch, Pongratz, *Z. physik. Chem.* **B-27**, 193 (1934). (9) von Auwers, Schmidt, *Ber.* **46**, 474 (1913) (10) Kuhn, F. Köhler, L. Köhler, *Z. physiol. Chem* **247**, 197–219 (1937); *Cent.* **1937**, II 2391; *C.A.* **31**, 6264 (1937).

(11) Fuson, Christ, Whitman, *J. Am. Chem. Soc.* **58**, 2450–2452 (1936). (12) von Auwers, Spiess, *Ber.* **34**, 191–192 (1901) (13) Brown, *J. Am. Chem. Soc.* **60**, 1325–1328 (1938). (14) Rupe, Schaerer, *Helv. Chim. Acta* **8**, 863 (1925). (15) Wedekind, *Ann.* **378**, 288 (1910). (16) von Auwers, Risse, *Ann.* **502**, 291–292 (1933). (17) Fieser, Hershberg, *J. Am. Chem. Soc.* **61**, 1280 (1939). (18) von Auwers, *Ann.* **439**, 150 (1924) (19) Ref. 7, pp. 97–100.

3:7695 5-CHLORO-2-METHYLPENTANE $C_6H_{13}Cl$ Beil. I —
(Isohexyl chloride) I_1-(53)
I_2—



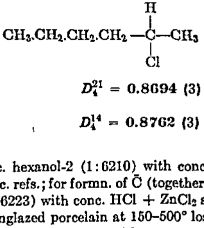
B.P. 125–126° at 761 mm. (1)

[For prepn. of C̄ from N-(benzoyl)isohexylamine with PCl_5 followed by aq. see (1).]

C̄ on htg. in alc. with diethyl sodiomalonate in a s.t. at 100° for 4 hrs. gives an ester from which 2-methyloctanoic acid-8, b.p. abt. 230°, was obtd. by conventional methods (1).

3:7695 (1) Clarke, *J. Chem. Soc* **103**, 1699 (1913).

3:7715 2-CHLOROHEXANE $C_6H_{13}Cl$ Beil. I - 144
(*sec.*-(2)-Hexyl I_1-(52)
chloride; n-butyl- I_2-(100)
methyl-carbinyl chloride)



B.P. 125–127°	**(1)**	D_4^{21} = **0.8694 (3)**	$n_D^{21.5}$ = **1.4142 (3)**
123–126°	**(2)**		
122.5° at 754 mm.	**(3)**	D_4^{14} = **0.8762 (3)**	
61° at 100 mm.	**(3)**		

[For prepn. of C̄ from corresp. alc. hexanol-2 (1:6210) with conc. HCl at 125° (90% yield (3)) or conc. HCl (1) (2) see indic. refs.; for formn. of C̄ (together with other products) from reaction of 2-ethylbutanol-1 (1:6223) with conc. HCl + $ZnCl_2$ see (4).]

C̄ on passing over Pyrex glass or unglazed porcelain at 150–500° loses HCl (5).

[For study of rate of reaction with KI in acetone see (2).]

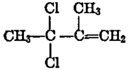
C̄ with Mg in dry ether gives RMgCl; upon treatment with oxygen this gives (4) hexanol-2 (1:6210) q.v.

Ⓓ **n-Butyl-methyl-acet-anilide: m.p. 91–92° u.c. (1).** [From C̄ via conversion to RMgCl and reaction with phenyl isocyanate (1).]

Crotylidene diacetate (from crotonaldehyde (1:0150) + Ac_2O in 95% yield (3)) gives (3) with dry HCl 3-chloro-1-acetoxybutene-1, b.p. 64° at 13 mm., $D_{20}^{20} = 1.083$, $n_D^{20} = 1.451$ (3), derived from the synionic isomer of C̄.

3:7685 (1) Kirrmann, *Compt. rend.* **199**, 1228–1229 (1934). (2) Kekulé, *Ann.* **162**, 98–100 (1872). (3) Kirrmann, *Bull. soc. chim.* (5) **5**, 917–918 (1938).

3:7690 3,3-DICHLORO-2-METHYLBUTENE-1 $C_5H_8Cl_2$ **Beil. S.N. 11**



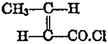
B.P. 124–126° at 762 mm. (1) D_4^{19} **= 1.085 (1)** n_C^{19} **= 1.4513 (1)**
55–57° at 60 mm. (1)

[For prepn. of C̄ from 3-chloro-2-methylbutene-2 (3:7335) with Cl_2 + $NaHCO_3$ at 0° see (1) (yield 80% together with 10% 2,3,3-trichloro-2-methylbutane (3:4755), m.p. 182–183° (1)).]

C̄ on htg. gives by allylic transposition 1,3-dichloro-2-methylbutene-2 (3:8170) (1).

3:7690 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939).

3:7693 α-CROTONOYL CHLORIDE C_4H_5OCl **Beil. II - 411**



II₁-(188)
II₂-(392)

B.P. 126°	(1)	D_4^{20} = **1.080** (9)	
124–126°	(2)		
124–125° at 759 mm.	(3)	D_-^{20} = **1.0905** (3)	
124–125°	(4) (5)		
124°	(6)		
123–124°	(7)	$D_4^{17.4}$ = **1.0822** (9)	$n_D^{17.9}$ = **1.46001** (9)
122.6–123.6°	(8)		
34–36° at 18 mm.	(3)		

The name crotonoyl chloride is employed to avoid possible confusion with 1-chlorobutene-2 (3:7205) often designated as crotonyl chloride because of its relationship to crotonyl alcohol (buten-2-ol-1).

[For prepn. of C̄ from α-crotonic acid (1:0425) with $SOCl_2$ (yield: 95% (5), 86% (11)) (6) (8) (10) in pet. ether (80% yield (2)), or with PCl_3 (84% yield (3)) (7) (4), or with PCl_5 (12), or with benzoyl chloride (3:6240) (yield: 72–80% (13)) see indic. refs.; for prepn. of C̄ from NaĀ with PCl_5 + $POCl_3$ (1), with PCl_3 in ether (26% yield (14)), or with $POCl_3$ (9) see indic. refs.; for prepn. of C̄ by distn. of isocrotonyl chloride see (12).]

C̄ with EtOH yields (4) (by addn. of the resultant HCl) ethyl β-chloro-*n*-butyrate (3:8373).

[C̄ on htg with NaĀ (3) or with Et_3N + C_6H_6 in the cold (15) gives (81% yield (3)) crotonic anhydride (1:1155), b p. 248°.]

[For reactn. of C̄ with methyl diazoacetate see (2), with NaN_3 see (6).]

[C̄ with $AlCl_3$ + C_6H_6 in CS_2 in light gives (61% yield (11)) (1) both phenyl propenyl ketone [Beil. VII-368, VII₁-(194)], b.p. 135–140° at 20 mm. (1), 90–95° at 2 mm. (11), n_D^{25} = 1.5475 (11) (corresp. 1,3-diphenyl-5-methylpyrazoline from ketone with phenyl-

3:7735 3-CHLOROHEXATETRAENE-1,3,4,5 C_6H_5Cl Beil. S.N. 14

$$CH_2{=}C{=}C{=}\underset{}{\overset{Cl}{\overset{|}{C}}}{-}CH{=}CH_2$$

B.P. 127° dec. at 760 mm. (1) D_4^{20} = 0.9997 (1) n_D^{20} = 1.5280 (1)
82° at 163 mm. (1)
55° at 54 mm. (1)

[For prepn. of C̄ from 1,4-dichlorohexatriene-2,3,5 (3:9304) with MeOH/KOH at 10–15° or with NaOMe in dry MeOH see (1).]

C̄ on cat. hydrogenation yields (1) n-hexane (1:8530).

C̄ on oxidn. with aq. $KMnO_4 + Na_2CO_3$ soln. for 10 hrs. at 35–45° gives (1) oxalic acid dihydrate (1:0445).

3:7735 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933).

3:7740 n-VALERYL CHLORIDE C_5H_9OCl Beil. II - 301, II_1—, II_2-(266)

$$CH_3.CH_2.CH_2.CH_2{-}\underset{\underset{Cl}{|}}{C}{=}O$$

B.P.				
127–128°	(1)	F.P. −110.0° (2)	D_4^{20} = 1.0004 (3)	n_D^{20} = 1.4207 (3)
127.2°	(2)			1.4200 (4)
126.9° at 756 mm.	(3)			
126° at 730 mm.	(4)			
124.8–126.8°	(5)			
125–127°	(6)			
123–127°	(7)			

[For prepn. of C̄ from *n*-valeric acid (1:1060) with PCl_5 (60% yield (8)), with PCl_3 (77% yield (9)) (1) or $PCl_3 + ZnCl_2$ (75% yield (8)), with $SOCl_2$ (yield: 92.5% (7), 84% (4), 77% (8)), with benzoyl chloride (3:6240) (84–76% yield (6)), or with oxalyl dichloride (3:5060) (95% yield (10)) see indic. refs.]

C̄ htd. with sodium *n*-valerate yields (11) *n*-valeric anhydride (1:1137), b.p. 218°.

[C̄ with EtMgBr gives (66% yield (4)) 3-ethylheptanol-3; C̄ + $AlCl_3$ treated at 0° with ethylene gives (74% yield (12)) (13) *n*-butyl β-chloroethyl ketone (1-chloro-heptanone-3), but its constants have not been reported.]

[C̄ with $AlCl_3$ and phenol yields (14) 56% *o*-(*n*-valeroyl)phenol, b.p. 130° at 10 mm., D^{24}_{-} = 1.0435, $n_D^{25.5}$ = 1.5309 (semicarbazone, m.p. 204–204.5°), and 29% *p*-(*n*-valeroyl)-phenol, cryst. from pet. ether, m.p. 63°, b.p. 197.5–198.5° at 10 mm. (benzoate, m.p. 92°).]

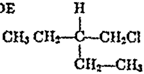
C̄ on hydrolysis yields *n*-valeric acid (1:1060), b.p. 186°. — For the amide, anilide, *p*-toluidide, α-naphthalide, and other derivs. corresp. to C̄ see *n*-valeric acid (1:1060).

[illegible] 833 (1895). (2) Timmermans, [illegible] *J. Chem. Soc.* **1936**, 162. (4) [illegible] ohlrausch, Pongratz, *Z. physik.* [illegible] –1328 (1938). (7) Fierz-David, [illegible] *Roy. Soc. Can.* III **27**, 97–103 [illegible] lich, Adams, *J. Am. Chem. Soc.* [illegible]

(11) Pickard, Kenyon, *J. Chem. Soc.* **101**, 1432 Note (1912). (12) Kenner, Statham, *Ber.* **69**, 17 (1936). (13) Schering-Kahlbaum Akt. Ges., Brit. 282,412, Feb. 15, 1928; *Cent.* **1929**, I 143. (14) Sandulesco, Girard, *Bull. soc. chim.* (4) **47**, 1308–1309 (1930).

3:7715 (1) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2119 (1934). (2) Conant, Hussey, *J. Am. Chem. Soc* **47**, 485 (1925). (3) Zelinskii, Przewalskii, *J. Russ. Phys.-Chem. Soc.* **40**, 1105–1123 (1908); *Cent* **1908**, I 1854. (4) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2535 (1938). (5) Farragher, Garner, *J. Am. Chem. Soc.* **43**, 1721 (1921).

3:7720 2-ETHYLBUTYL CHLORIDE $C_6H_{13}Cl$ **Beil. S.N. 10**
(1-Chloro-2-ethylbutane;
3-(chloromethyl)pentane)



B.P. 125–127° (1) D_4^{20} = **0.8914** (2) n_D^{20} = **1.4230** (2)
88° at 225 mm. (2)

[For prepn. of $\bar{C}$ from 2-ethylbutanol-1 (1:6223) with $SOCl_2$ + pyridine (82% yield) see (2); with 45% HCl in s.t. at 100° (11% yield) see (1). [Note that 2-ethylbutanol (1:6223) with conc. HCl + $ZnCl_2$ gives (2) by rearr. of the carbon chain 7 different chlorohexanes.]

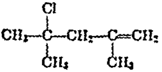
$\bar{C}$ on shaking at 79–87° for 7 hrs. with conc. HCl + $ZnCl_2$ rearranges in part to a mixt. of other hexyl halides (2).

$\bar{C}$ with Mg in dry ether gives RMgCl; upon treatment with oxygen this yields (2) 2-ethylbutanol-1 (1:6223) q.v.

Ⓓ β-Ethylvaleranilide: m.p. 83–84° (2) [From $\bar{C}$ via conversion to RMgCl and reaction with phenyl isocyanate; so prepared, m.p. 80.5–81.5° (2).]

3:7720 (1) Fourneau, Matti, *J pharm chim* (8) **14**, 513–522 (1931), *Cent* **1932**, I 2587. (2) Whitmore, Karnatz, *J. Am. Chem. Soc* **60**, 2533–2536 (1938).

3:7725 *d,l*-4-CHLORO-2,4-DIMETHYLPENTENE-1 $C_7H_{13}Cl$ **Beil. I - 220**
I_1—
I_2—

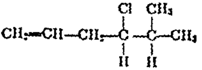


B.P. 126–128° (1)
45–48° at 40 mm. (1)

[For prepn of $\bar{C}$ from ethyl β-chloroisovalerate + MeMgBr in ether see (1).]

3:7725 (1) Lemaire, *Bull acad roy. Belg.* **1909**, 83–159; *Cent.* **1909**, I 1992; *C.A.* **4**, 1483–1484 (1910), *Rec. trav. chim.* **29**, 51–52 (1910).

3:7730 *d,l*-4-CHLORO-5-METHYLHEXENE-1 $C_7H_{13}Cl$ **Beil. I - 220**
d,l-3-Chloro-2-methylhexene-5
(Allyl-isopropyl-carbinyl chloride)
I_1—
I_2—



B.P. 125–130° dec. (1)

[For prepn of $\bar{C}$ from 2-methylhexen-5-ol-3 (allyl-isopropyl-carbinol) [Beil. I-447] with PCl_5 see (1).]

3:7730 (1) Fournier, *Bull. soc. chim.* (3) **15**, 886 (1896).

$\bar{C}$ on htg. in s.t. at 140–160° yields (29) 1,2-dichloropropane (3:5200) + acetone (1:5400); $\bar{C}$ similarly htd. with aq. yields (29) acetone (1:5400) + propionaldehyde (1:0110). — $\bar{C}$ on htg. with P_2O_5 yields (5) allyl chloride (3:7035) + 1-chloropropene-1 (3:7035).

$\bar{C}$ with aq. alk. readily gives (30) by loss of HCl and ring closure 1,2-epoxypropane (propylene oxide) (1:6115), b.p. 35°. [For study of rate of reactn. see (10) (31).]

$\bar{C}$ on oxidn. with CrO_3 yields (17) (14) (18) (5) (7) chloroacetone (3:5425) + AcOH (1:1010); $\bar{C}$ treated with $Ca(OCl)_2$ in cold, then warmed, yields (32) chloroform (3:5050) + AcOH (1:1010); $\bar{C}$ on oxidn. with HNO_3 yields chloroacetic acid (3:1370) + AcOH (1:1010) + oxalic acid (1:0445).

[For reactn. of $\bar{C}$ with Na_2S yielding (9) (33) β,β'-dihydroxy-di-*n*-propyl sulfide; with Me_3N in C_6H_6 on htg. in s.t. 8 hrs. at 100° giving (48% yield (34)) β-methylcholine chloride, m.p. 165° (34); with alkyl sulfates + alk. (35) to yield monoalkyl ethers of propylene glycol; with alkyl sulfates to yield (35) (36) β-chloroisopropyl alkyl ethers; with Br_2 + P to yield (8) 1-bromo-2-chloropropane, b.p. 117.5–118° at 756 mm., $D_4^{20} = 1.537$, $n_D^{20} = 1.47447$ (8), see indic. refs.]

—— **β-Chloroisopropyl acetate:** b.p. 149–150° (3) (2). [From $\bar{C}$ + AcCl (3).]

—— **β-Chloroisopropyl benzoate:** no b.p. recorded; $D_{19}^{19} = 1.172$ (14). [From $\bar{C}$ on htg. with BzCl at 180° (14); is saponified with great ease by alk. yielding propylene oxide (1:6115), b p. 35°.]

—— **β-Chloroisopropyl *p*-nitrobenzoate:** unreported.

Ⓓ **β-Chloroisopropyl 3,5-dinitrobenzoate:** m.p. 76.5–77.3° (38).

Ⓓ **1-(Phthalimido)propanol-2** [*N*-(β-hydroxy-*n*-propyl)phthalimide: m.p. 88–89° (39), 90–91° (40). [From $\bar{C}$ + K phthalimide in s.t. at 170° for 3 hrs. (39); see also under corresp. deriv. of 2-chloropropanol-1 (3:7917).]

3:7747 (1) Dewael, *Bull. soc. chim. Belg.* **33**, 504 (1924). (2) Henry, *Rec. trav. chim.* **22**, 209–210. 326–329 (1903). (3) Bancroft, *J. Am. Chem. Soc.* **41**, 426–427 (1919). (4) Henry, *Bull. acad, roy. Belg.* **1902**, 535–536; *Cent.* **1902**, II 1093–1094. (5) Michael, *Ber.* **39**, 2786–2789 (1906). (6) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) **147**, 237 (1936). (7) Henry, *Bull. acad. roy. Belg.* **1903**, 397–431; *Cent.* **1903**, II 486. (8) Dewael, *Bull. soc. chim. Belg.* **39**, 87–90 (1930). (9) Coffey, *J. Chem. Soc.* **119**, 96–97 (1921). (10) Smith, *Z. physik. Chem.* **93**, 59–85 (1919).

(11) Oppenheim, *Ann. Suppl.* **6**, 367–369 (1868). (12) Michael, *J. prakt. Chem.* (2) **60**, 420–423 (1899). (13) Oser, *Ann. Suppl.* **1**, 254 (1861). (14) Morley, Green, *J. Chem. Soc.* **47**, [illegible] Taurke, *Ber.* **38**, 1669 (1905). (16) Britton, Cole- [illegible] 227, Jan. 8, 1935; *Cent.* **1935**, II 350; *C.A.* **29**,1432 [illegible] –252 (1870). (18) Michael, *J. prakt. Chem.* (2) [illegible] .), Canadian 285,920, Dec. 25, 1928; *Cent* **1932**, I 1153. (20) Tropsch, Kassler, Brit. 377,595, Aug. 18, 1932; *Cent.* **1932**, II 2724.

(21) Henry, *Rec. trav. chim.* **26**, 138 (1907); *Bull. acad. roy. Belg.* **1906**, 523–557; *Cent.* **1906**, II 1550–1551. (22) Britton, Nutting, Huscher (to Dow Chem. Co), U.S. 2,130,226, Sept. 13, [illegible], Apr. [illegible] (24) [illegible] 2053. [illegible] Smith, [illegible] 1,918,- [illegible] *Phys*- [illegible] (5) **4**, 281–295 (1937).

(31) Smith, *Z. physik. Chem.* **A-152**, 153–156 (1931). (32) Ssuknewitsch, Tschilingarjan, *Ber.* **69**, 1542 (1936). (33) Farbwerke Meister, Lucius Brüning, Brit. 185,403, Oct. 25, 1922; [illegible] 246–247 (1932). (35) Davidson [illegible]; *C.A.* **23**, [illegible] Kaplan, [illegible] 12 (1935). [illegible] 7 (1917).

3:7745 ETHOXYACETYL CHLORIDE

$C_4H_7O_2Cl$ Beil. III - 240

$C_2H_5O.CH_2.CO\ Cl$ III₁-(92) III₂-(173)

B.P. 127–128°	(1) (2)	D_4^{20} = 1.1170 (4) n_D^{20} = 1.42030 (4)
123–124°	(3)	
49–50° at 37 mm.	(4)	

Colorless limpid liq. with strong odor and lachrymatory character; fumes in moist air.

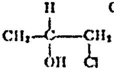
[For prepn. from ethoxyacetic ac. (1:1070) by actn. of PCl_3 (90% yield (2)) see (1) (2); by actn. of thionyl chloride (90% yield (5), 73% yield (3), 45% yield (4)) see (3) (4) (5) (6).]

Ċ in aq. sinks to bottom in oily drops which soon dissolve by hydrolysis to ethoxyacetic acid (1:1070) + HCl.

3:7745 (1) Henry, *Ber.* **2**, 276–277 (1869). (2) Pratt, Robinson, *J. Chem. Soc.* **123**, 752, footnote (1923). (3) Rothstein, *Bull. soc. chim.* (4) **51**, 841–842 (1932). (4) Leimu, *Ber.* **70**, 1050 (1937). (5) Sommelet, *Ann. chim.* (8) **9**, 492–493 (1906); *Bull. soc. chim.* (4) **1**, 365–369 (1907). (6) Jones, Powers, *J. Am. Chem. Soc.* **46**, 2528 (1924).

3:7747 *dl*-1-CHLOROPROPANOL-2

(Propylene α-chlorohydrin; β-chloro-isopropyl alcohol; chloromethyl-methyl-carbinol)



C_3H_7OCl Beil. I - 363 I₁-(185) I₂-(383)

B.P.		
127–128°	at 761 mm. (1) (14)	D_{20}^{20} = 1.115 (5) n_D^{20} = 1.43924 (2)
127°	(13)	1.111 (2)
126–127° cor.	at 762 mm. (2) (3) (21)	
126–127°	at 760 mm. (4)	
120.0–120.5° cor.	at 722 mm. (5)	
78–81°	at 80 mm. (6)	

[*See also* 2-*chloropropanol*-1 (3:7917).]

Colorless liq. forming with aq. a const.-boilg. mixt., b.p. 96° at 743 mm., contg. 49.1 wt. % = 15.15 mole % Ċ (37).

[For prepn. of Ċ from allyl chloride (3:7035) by addn. of H_2O to the unsatd. linkage through the actn. of H_2SO_4 + $CuSO_4$ as specified (yield 66–70% (8)) (9) (3) (5) (2) (11) see indic. refs.; an extensive study (10) has shown that this is the only method of prepn. of Ċ which does not give also some 2-chloropropanol-1 (propylene β-chlorohydrin (3:7917).]

[For prepn. of ordinary Ċ (probably containing some of the isomer) from propanediol-1,2 (propylene glycol) (1:6455) with HCl (2) (12) (10), with S_2Cl_2 (14) (10), or with SCl_2 (15) see indic. refs.; from propylene glycol diacetate with an alc. + HCl see (16); from propylene with HOCl (17) (18) (19) (20) (10) (21), with Cl_2 + aq. (22) (23) (30), or with tert-butyl hypochlorite (3:7160) (24) see indic. refs.; from 1,2-epoxypropane (propylene oxide) (1:6115) with HCl see (12) (1) (2) (7) (25) (10), note, however, that by these methods there results an inseparable mixt. of much Ċ with a little 2-chloropropanol-1 (3:7917) (10).]

[For prepn. of Ċ from chloroacetone (3:5425) with $AlEt_3$ ethylate (77% yield (4)) or by actn. of yeast (26), from 2-amino-1-chloropropane with nitrous acid (27) or from 1,2-dichloropropane (propylene dichloride) (3:5270) with [illegible] followed by hydrolysis (28) see indic. refs.]

3:0565 (1) Kunckell, Johannssen, *Ber.* **30**, 1714–1715 (1897). (2) Mannich, Drauzburg, *Arch. Pharm.* **250**, 534 (1912). (3) Morel, *Bull. soc. chim.* (3) **21**, 958–964 (1899). (4) Morel, *Bull. soc. chim.* (3) **21**, 964–966 (1899). (5) Nencki, *Ber.* **26**, Ref., 588 (1893). (6) Prevost, *J. prakt. Chem.* (2) **4**, 379–380 (1871). (7) Fries, Pfaffendorf, *Ber.* **43**, 214–215 (1910). (8) Bakunin, *Gazz. chim. ital.* **30**, II 358 (1900). (9) van der Stichele, *J. Chem. Soc.* **123**, 1228 (1923). (10) von Auwers, Mauss, *Ber.* **61**, 419 (1928).
(11) Barnett, Cook, *J. Chem. Soc.* **121**, 797 (1922).

3:0572 DI-(β-CHLOROETHYL) OXALATE $C_6H_8O_4Cl_2$ **Beil. S.N. 170**

$CO.O.CH_2.CH_2Cl$
|
$CO.O.CH_2.CH_2Cl$

M.P. 45° (1) B.P. 132° at 3 mm. (2)

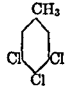
[For prepn. of C̄ from ethylene chlorohydrin (3:5552) with anhydrous oxalic acid (1:0535) by satn. with HCl gas and htg. at 100° see **(1)**.]

[C̄ with Me_3N in C_6H_6 gives **(1)** "oxalylcholine chloride," $C_{12}H_{26}O_4N_2Cl_2$, very hygroscopic cryst. ndls. (chloroaurate, m.p. 250.5° dec.).]

[C̄ + C_6H_6 + $AlCl_3$ gives **(2)** bibenzyl (1:7149) + tar.]

3:0572 (1) Contardi, Ercoli, *Atti IX congresso intern. chim. Madrid* **9**, V, 163–173 (1934); *Cent.* **1936**, II 3903–3904; *C.A.* **31**, 1764 (1937). (2) Markarov-Zemlyanskii, Korshak, Savenkov, *J. Gen. Chem.* (*U.S.S.R.*) **11**, 331–334 (1941); *Cent.* **1942**, I 993; *C.A.* **35**, 5883 (1941).

3:0580 3,4,5-TRICHLOROTOLUENE $C_7H_5Cl_3$ **Beil. V - 299**
V_1—
V_2—



M.P. 44.5–45.5° (1) B.P. 245.5–247° at 768 mm. (2)
42.5° (2)

Readily volatile with steam.

[For prepn. of C̄ from 3,5-dichloro-4-aminotoluene [Beil. XII-990] or from 4,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of Cu_2Cl_2 reactn. see **(1)**; from potassium salt of 3,4,5-trichlorotoluenesulfonic acid-2 by hydrolysis with strong H_2SO_4 see **(2)**.]

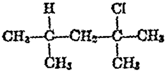
[C̄ with Cl_2 in pres. of Al/Hg yields **(3)** 2,3,4,5-tetrachlorotoluene (3:2710), m.p. 97–98° **(3)**.]

C̄ on mononitration with cold fumg. HNO_3 **(1)** yields 3,4,5-trichloro-2-nitrotoluene [Beil. V-333], pr. from alc., m.p. 81–82° **(1)**; C̄ on dinitration with a mixt. of 6 pts. fumg. HNO_3 and 4 pts. conc. H_2SO_4 **(1)** yields 3,4,5-trichloro-2,6-dinitrotoluene [Beil. V-346], ndls. from AcOH, m.p 163–164° **(1)**.

C̄ on oxidn. with dil HNO_3 in s.t. at 130° readily yields **(1)** 3,4,5-trichlorobenzoic acid (3:4920), m.p. 203° **(1)**.

3:0580 (1) Cohen, Dakin, *J. Chem. Soc.* **81**, 1336–1339 (1902). (2) Wynne, *J. Chem. Soc.* **61**, 1070–1071 (1892). (3) Cohen, Dakin, *J. Chem. Soc.* **89**, 1454 (1906).

3:7750 2-CHLORO-2,4-DIMETHYLPENTANE $C_7H_{15}Cl$ Beil. I —
(Dimethyl-isobutyl-carbinyl chloride) I_1-(59)
I_2—



B.P. 127–128° dec. at 733 mm. (1)	D_4^{20} = **0.861** (1)	n_D^{20} = **1.4180** (1)
126–127° (2)		**1.4239** (3)
33–34° at 20 mm. (3)	D_4^{10} = **0.8650** (2)	$n_D^{16.5}$ = **1.4202** (2)

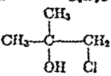
[For prepn. of C̄ from 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol) [Beil. I-417, I_1-(207), I_2-(446)] by saturation with HCl (2) or as by-product during its reactn. with $AlCl_3 + C_6H_6$ (3) see indic. refs.; for prepn. of C̄ from 2,4-dimethylpentanol-3 (di-isopropyl-carbinol) (1:6215) in 100% yield by saturation with HCl gas and stdg. 10 weeks at 20° (note rearrangement) (1).]

C̄ with Mg in dry ether gives (1) RMgCl, which upon oxidation with O_2 and subsequent hydrolysis gives 32% yield 2,4-dimethylpentanol-2 (dimethyl-isobutyl-carbinol), b.p. 130–131° at 738 mm., D_4^{20} = 0.811, n_D^{20} = 1.4166 (1).

[For reactn. of C̄ with $AlCl_3 + C_6H_6$ yielding 2,4-dimethyl-2-phenylpentane, b.p. 218°, D_4^{15} = 0.8741, $n_D^{15.5}$ = 1.49383, see (2).]

3:7750 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2267 (1938). (2) Schreiner, *J. prakt. Chem.* (2) **82**, 294 (1910). (3) Huston, Fox, Binder, *J. Org. Chem.* **3**, 252–253 (1939).

3:7752 1-CHLORO-2-METHYLPROPANOL-2 C_4H_9OCl Beil. I - 382
(Chloro-*ter*-butyl alcohol; I_1—
chloro-trimethylcarbinol; I_2-(416)
isobutylene α-chlorohydrin,
α,α-dimethylethylene α-chlorohydrin)



B.P.			M.P.	
128–129°		(1) (2)	**−20°** (5)	D_4^{20} = **1.0628** (9)
127–129°		(3)		
127–128.5°		(4)		
126–128°		(5) (6) (7)		
126–127°	at 736.4 mm.	(8)		
126.7°		(9)		
126.0–126.5°	at 748.3 mm.	(10)		
71.0–71.5°	at 100 mm.	(10)		

[*See also* 2-*chloro*-2-*methylpropanol*-1 (3:7905).]

Colorless liq. somewhat sol. aq.; 100 g. aq. at 20° dis. 18.6 g. C̄ (note also that 100 g. C̄ at 20° dis. 19 g. H_2O) (9). — C̄ forms with aq. a const.-boilg. mixt., b.p. 93–94° at 760 mm., contg. 34% aq. (9).

[For prepn. of C̄ from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) or from 1-chloro-2-methylpropene-1 (β,β-dimethylvinyl chloride) (3:7120) by cat. hydration of their unsatd. linkage (63–66% yield) see (9) (11); note that the former with 80% H_2SO_4 at 0° or the latter with 90% H_2SO_4 at −10° to 0° stirred for 2½ hrs., poured onto ice, and distilled gives 63–66% of the initial chloride as C̄; note that other acids can also be used for this hydration, e.g., 85% H_3PO_4, 70% HNO_3, 60% $HClO_4$, benzenesulfonic acid, etc., each having its own optimum conditions (9); note also that in this process some 32–18%

respectively of the initial chloride is not hydrated but partially isomerized to a mixt. contg. 90% β,β-dimethylvinyl chloride (3:7120) + 10% methallyl chloride (3:7145) irrespective of whichever one was initially employed (9).]

[For prepn. of $\bar{C}$ from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) by liq.-phase hydrolysis of the more reactive halogen atom under neutral (or even slightly acidic or basic) conditions (best yield 48% by refluxing 18 hrs. with aq.) see (10).]

[For prepn. of $\bar{C}$ from chloroacetone (3:5425) or ethyl chloroacetate (3:5700) with MeMgBr (yields: 60% (5), 38% (12)) (3) (6) or MeMgI (20% yield (4)) see (3) (5) (6) (12) (note that $\bar{C}$ is accompanied (as a result of reaction of a second MeMgBr (13) (14)) by *some 2-methylbutanol-2 (1:6160)); for prepn.* of $\bar{C}$ from isobutylene with HOCl (yields: 64% (6), 63% (1), 60% (7), 47% (2)) (5) (15), with $Cl_2 + H_2O$ (16) (17) in pres. of 10% $CuCl_2$ (80–85% yield (24)), or with *ter*-butyl-hypochlorite (3:7165) (18) see indic. refs.; for formn. of $\bar{C}$ from 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117) with HCl gas in ether see (19) (6) (4) (1) (note, however, that the prod. is a mixt. consisting of about ⅔ $\bar{C}$ contaminated with about ⅓ of the isomeric 2-chloro-2-methylpropanol-1 (3:7905)).]

[For formn. of $\bar{C}$ from 1-amino-2-methylpropanol-2 hydrochloride with conc. HCl in s.t. at 100° see (12).]

[$\bar{C}$ on reduction with Na/Hg in dil. HCl yields (2) (15) 2-methylpropanol-1 (isobutyl alcohol) (1:6165); this unexpected result presumably is due to intermediate formation of isobutylene oxide (1:6117) which on reduction opens the ring to give isobutyl alc. (not *ter*-butyl alcohol).]

[$\bar{C}$ on protracted oxidation, e.g., with mixt. of 1.5 wt. pts. fumg. HNO_3 + 3 5 wt. pts. conc. HNO_3 at 75° for 20 hrs. (2), gives traces of chloroacetone (3:5425) and a little oxalic acid (1:0445) and α-chloroisobutyric acid (3:0235) (5).]

$\bar{C}$ on refluxing with aq. is slowly (e.g., 56% in 14 hrs. (2)) (21) converted to isobutyraldehyde (1:0120); note that this reaction carried out above 100° under press. (20) is greatly accelerated.

[$\bar{C}$ with warm conc. HCl yields (10) (5) 1,2-dichloro-2-methylpropane (3:7430).]

$\bar{C}$ on solution in cold 45% H_2SO_4 followed by warming loses H_2O and yields (9) a mixt. consisting of about 90% 1-chloro-2-methylpropene-2 (methallyl chloride (3:7145)) accompanied by about 10% 1-chloro-2-methylpropene-1 (β,β-dimethylvinyl chloride) *(3:7120); a mixt. of these two chlorides has also been obtd. by use of* P_2O_5 (1) (2) or anhydrous oxalic acid (2) (22).]

[$\bar{C}$ added dropwise to dry powdered KOH, NaOH, CaO, or $Ca(OH)_2$ loses HCl and gives (95% yield using NaOH (10), 67% using KOH (6)) 1,2-epoxy-2-methylpropane (isobutylene oxide) (1:6117), b.p. 56.0–56.5° cf. (24).]

[$\bar{C}$ with aq. alkali ultimately yields 2-methylpropanediol-1,2 (isobutylene glycol) (1:6446) or its polymerization products; for study of kinetics of reaction of $\bar{C}$ with aq. alk. see (4) (8).]

[$\bar{C}$ with KCN in 4 vols. 80% alc. refluxed for 15–20 min. gives (45–50% yield (23)) β-hydroxy-isovaleronitrile [Beil. III-328], b.p. 210–212° at 756 mm., 130–132° at 30 mm., f p. −12°, $D_{-}^{20} = 0.96762$, $n_D = 1.42911$ (23).]

[$\bar{C}$ with aq. 23% $EtNH_2$ (4 moles) in s.t. at 100° for 8 hrs. gives (70–75% yield (25)) 1-(ethylamino)-2-methylpropanol-2, b.p. 156° ($\bar{B}$.HCl, m.p. 151° (25)). — $\bar{C}$ with aq. Et_2NH refluxed 3–4 hrs. gives (60% yield (26)) 1-(diethylamino)-2-methylpropanol-2, b.p. 164–165° at 761 mm. (26), $D_4^{20} = 0.8382$ (27), $n_D^{20} = 1.4253$ (27) ($\bar{B}$.PkOH, m.p. 99–100° (26)).— For reactn. of $\bar{C}$ with *N*-methylaniline, *N*-ethylaniline, or di-*n*-butylamine see (27).]

—— **Chloro-*ter*-butyl acetate:** b.p. 154° at 760 mm. (28), 153–154° (5), $D_4^{15} = 1.0626$ (28), $n_D^{15} = 1.4340$ (28). [From $\bar{C}$ + AcCl (5); also indirectly (28% yield (28)) from

isobutylene + N,N'-dichlorourea in AcOH.] — [For analogous indirect prepn. of the formate, chloroacetate, and trichloroacetate see (28).]

—— Chloro-*ter*-butyl benzoate: unreported.

—— Chloro-*ter*-butyl *p*-nitrobenzoate: unreported.

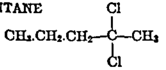
—— Chloro-*ter*-butyl 3,5-dinitrobenzoate: unreported.

Ⓓ 1-(*N*-Phthalimido)-2-methylpropanol-2 (*N*-(α-hydroxyisobutyl)phthalimide): ndls. or lfts. from alc., m.p. 106–107° (12). [From C̄ + K phthalimide in s.t. at 150° for 4 hrs. (60% yield (12)).]

3:7752 (1) Michael, Leighton, *J. prakt. Chem* (2) **64**, 103–104 (1901). (2) Michael, Leighton, *Ber.* **39**, 2157–2163 (1906). (3) Tiffeneau, *Compt. rend.* **134**, 775 (1902). (4) Nillson, Smith, *Z. physik. Chem.* **A-166**, 143–144 (1933). (5) Henry, *Rec. trav. chim.* **26**, 142–151 (1907); *Bull. acad. roy. Belg.* **1906**, 523–557; *Cent.* **1906**, II 1550–1551; *Compt. rend.* **142**, 131, 494–496 (1906). (6) Krassusky, *J. prakt. Chem.* (2) **75**, 241–247 (1907). (7) Krassusky, *J. Russ. Phys.-Chem. Soc.* **33**, 1–26 (1901); *Cent.* **1901**, I 995–997. (8) Evans, *Z. physik. Chem.* **7**, 338–357 (1891). (9) [illegible] –388 (1941). (10) Sparks, Nelson, *J. Am.* [illegible] U.S. 2,042,222, May 26, 1936; *Cent.* **1937**, I [illegible] Petroleum Maatschappij, French 791,644, [illegible], *Ber.* **54**, 3158–3160 (1921). (13) Henry, [illegible] feneau, *Compt. rend.* **145**, 438 (1907). (15) Butlerow, *Ann.* **114**, 25–26 (1867). (16) Kautter, U.S. 2,060,086, Oct. 17, 1936; *Cent.* **1937**, I 3873; N. V. de Bataafsche Petroleum Maatschappij, French 799,805, June 20, 1936, *Cent.* **1936**, II 3468; *C.A.* **30**, 8250 (1936). (17) Britton, Nutting, Huscher (to Dow Chem. Co), U.S. 2,130,226, Sept. 13, 1938; *Cent.* **1939**, I 1856; *C.A.* **32**, 9096 (1938). (18) N. V. de Bataafsche Petroleum Maatschappij, French 740,350, Jan. 24, 1933; *Cent.* **1933**, I 2870. (19) Michael, Leighton, *Ber.* **39**, 2789–2795 (1906). (20) Groll, Kautter (to Shell Development Co), U.S. 2,042,225, May 26, 1936; *Cent.* **1937**, I 184; *C.A.* **30**, 4872 (1936); Canadian 363,685, Jan. 26, 1937; *Cent.* **1937**, II 1661.

(21) Krassusky, *Bull. soc. chim.* (3) **24**, 236 (1900). (22) Krassusky, *J. prakt. Chem.* (2) **64**, 389–390 (1901). (23) Lemaire, *Rec. trav. chim* **29**, 58–60 (1910); *Bull. acad roy. Belg.* **1909**, 83–159, *Cent.* **1909**, I 1982. (24) Moureu, Dodé, *Bull. soc. chim.* (5) **4**, 286–289 (1937). (25) Krassusku, Kutzenos, *Ukrain. Khem. Zhur* **4**, Sci. Pt., 75–77 (1929); *Cent* **1929**, II 2174, *C.A.* **24**, 1083 (1930). (26) Krassusky, Stepanoff, *J. prakt Chem.* (2) **115**, 321–324 (1927). (27) K. N. Campbell, B. K. Campbell, *Proc. Indiana Acad. Sci.* **49**, 101–104 (1939); *C.A.* **35**, 5460 (1941). (28) Likhosherstov, Petrov, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 2000–2008 (1939); *C.A.* **34**, 4381 (1940).

3:7755 2,2-DICHLOROPENTANE $C_5H_{10}Cl_2$ Beil. I - 131 I_1— I_2-(95)



B.P. 128–129° cor. (1)
44° at 31 mm. (1)
36–37° at 20 mm. (1)

D^{20}_{-} = **1.040** (1) n_D^{20} = **1.434** (1)

The prod. upon which the above data are based was admittedly impure, still contg. 20% 2,3-dichloropentane (3:8010) q.v.

[For prepn. of C̄ from methyl *n*-propyl ketone (1:5415) with PCl_5 see (1) (2) (3); for formn. of C̄ (together with other products) from pentane (1:8505) + Cl_2 see (4).]

C̄ with alc. KOH gives (2) 2-chloropentene-1 (3:7280) and pentyne-1 (1:8025). — C̄ on boilg. with $NaNH_2$ in xylene gives (1) pentyne-1 (1:8025).

[For reactn. of C̄ with SbF_3 yielding 2,2-difluoropentane, b.p. 59.8°, D_4^{20} = 0.8958, n_D^{20} = 1.33570, see (3).]

3:7755 (1) Bourgeul, *Ann. chim.* (10) **3**, 220, 368–370 (1925); *Bull. soc. chim.* (4) **35**, 1634 (1924). (2) Bruylants, *Ber.* **8**, 411 (1875). (3) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* **61**, 938–940

(1939). (4) Lemke, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1995–1998 (1937); *Cent.* **1939**, I 2397; *C.A.* **32**, 482 (1938).

3:7760 ISOBUTYL CHLOROFORMATE $C_5H_9O_2Cl$ Beil. III - 12
(Isobutyl chlorocarbonate) $(CH_3)_2CH.CH_2\,O.CO.Cl$ III_1-(6)
III_2-(11)

B.P. 128.8° cor. (1) (2) $D_4^{17.9}$ = **1.0425** (3) $n_{He}^{17.9}$ = **1.40711** (3)
$D_{15}^{18.5}$ = **1.0445** (4)

Colorless mobile lachrymatory oil. — Insol in aq. and only slowly hydrolyzed by it even on htg.

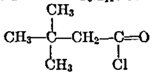
[For prepn. of C̄ (35% yield (2)) from isobutyl alc. (1:6165) + phosgene (3:5000) see (1) (2) (5).]

Ⓓ **Isobutyl carbamate** [Beil. III-29]: from C̄ in C_6H_6 by treatment with NH_3 gas, filtration of pptd. NH_4Cl, and evapn. of solvent; lfts. from aq., m.p. 61° (6); 64.4° (7); 64–65° (8).

Ⓓ **Isobutyl *N*-phenylcarbamate** (isobutyl carbanilate) [Beil. XII-321]: from C̄ in ether by treatment with ether soln. of aniline (1 mole) + pyridine (1 mole); ndls. from alc., m.p. 86° (9) (10).

3:7760 (1) Roese, *Ann.* **205**, 230 (1880). (2) Hamilton, Sly, *J. Am. Chem. Soc.* **47**, 436–437 (1925). (3) von Auwers, *Ber.* **60**, 2140 (1927). (4) Dobrosserdow, *Cent* **1911**, I 955 (5) Hochstetter, Ger. 254,471, Feb. 16, 1915; *Cent.* **1915**, I 464. (6) Thiele, Dent, *Ann.* **302**, 271 (1898). (7) Brunel, *Ber.* **44**, 1002 (1911). (8) Schmidt, *Z. physik. Chem.* **58**, 514 (1907). (9) Michael, Cobb, *Ann* **363**, 84 (1908). (10) Huckel, Ackermann, *J. prakt. Chem.* (2) **136**, 23 (1933).

3:7880 β,β-DIMETHYL *n*-BUTYRYL CHLORIDE $C_6H_{11}OCl$ Beil. S.N. 162
(*ter*-Butylacetyl chloride)



B.P. 128.5–130.3°	at 746 mm. (1)	D_4^{20} = **0.9696** (1)	n_D^{20} = **1.4230**	(6)
79.5°	at 165 mm. (2)	**0.968** (3)	**1.4226**	(5)
79–81°	at 150 mm. (3)		**1.422**	(1), (3)
79	at 150 mm. (4)		**1.4213**	(2)
68°	at 100 mm. (5)		**1.4212**	(4)
51°	at 44 mm. (6)	D_4^0 = **0.9872** (1)		

[For prepn. of C̄ from *ter*-butylacetic acid (1:1112) with $SOCl_2$ (1) (yields: 93% (3), 86% (4) (5), 84% (2)) see indic. refs.]

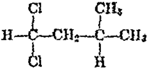
[For reactn. of C̄ with various alcs. to give corresp. alkyl *ter*-butylacetates see (2) (3) (7):
126.5° at 739 mm. (3), 128° at 735 mm. (2), D_4^{20} = 0.8710
, ethyl *ter*-butylacetate, b.p. 144.5–144.7° at 739 mm. (3),
3).]

[For behavior of C̄ with a large excess of various Grignard compounds see following refs.: with EtMgBr (5), *n*-PrMgBr (5), *iso*-PrMgBr (2), *n*-BuMgBr (5), *iso*-BuMgBr (2), *ter*-BuMgCl (4) (6), *n*-AmMgBr (5).]

C̄ on hydrolysis yields *ter*-butylacetic acid (1:1112) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to C̄ see 1:1112).

3:7880 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Whitmore, Foster, *J. Am. Chem. Soc.* **64**, 2966–2968 (1942). (3) Homeyer, Whitmore, Wallingford, *J. Am. Chem. Soc.* **55**, 4211–4212 (1933). (4) Whitmore, Heyd, *J. Am. Chem. Soc.* **60**, 2030–2031 (1938). (5) Whitmore, Popkin, Whitaker, Mattel, Zech, *J. Am. Chem. Soc.* **60**, 2462–2464 (1938). (6) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* **63**, 643–654 (1941). (7) Whitmore, Homeyer (to Mallinckrodt, Chem. Works), U.S. 2,052,995, Sept. 1, 1936; *Cent.* **1936**, II 3846; *C.A.* **30**, 7125 (1936).

3:7885 *d,l*-**4,4-DICHLORO-2-METHYLBUTANE** $C_5H_{10}Cl_2$ Beil. I - 135
I_1-(47)
I_2—



B.P. 130° (1)
129.9–131.5° (2)
128–130° (3)

$D_4^{22} = 1.05$ (1)

Colorless limpid liquid, insol. aq., sol. in alc. or ether.

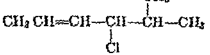
[For prepn. of $\bar{C}$ from isovaleraldehyde (1:0140) with PCl_5 see (1) (2) (3); for formn. of $\bar{C}$ by actn. of Cl_2 ($+I_2$) on diisoamyl sulfide see (4).]

$\bar{C}$ with KOH gives (1) (3) 4-chloro-2-methylbutene-3 (3:7215) and ultimately 3-methylbutyne-1 (isopropylacetylene) (1:8010), b.p. 28°.

$\bar{C}$ htd. with PbO + H_2O gives (4) isovaleraldehyde (1:0140).

3:7885 (1) Ebersbach, *Ann.* **106**, 265–266 (1858). (2) Kohlrausch, *Monatsh.* **65**, 197 (1935). (3) Bruylants, *Ber.* **8**, 413–414 (1875). (4) Spring, Lecrenier, *Bull. soc. chim.* (2) **48**, 627 (1887).

3:7890 *d,l*-**4-CHLORO-5-METHYLHEXENE-2** $C_7H_{13}Cl$ Beil. I —
(*d,l*-3-Chloro-2-methylhexene-4) I_1—
I_2-(108)



B.P. 130° (1)
38–40° at 8 mm. (2)

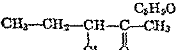
[For prepn. of $\bar{C}$ from 2-methylhexen-4-ol-3 [Beil. I-447, I_2-(489)] with conc. HCl at ord. temp. (90% yield (2)) or with $SOCl_2$ in pet. ether (1) see indic. refs.]

[$\bar{C}$ with quinoline loses HCl on boilg. giving (1) 2-methylhexadiene-2,4 [Beil. I-257, I_2-(235)], b.p. 99° (1).]

[$\bar{C}$ with diethylamine yields (3) 3-diethylamino-2-methylhexene-4, oil, b.p. abt. 175° (3).]

3:7890 (1) Staudinger, Muntwyler, Ruzicka, Seibt, *Helv. Chim. Acta* **7**, 399 (1924). (2) Böttcher (to I.G.), Ger. 508,891, Oct. 2, 1930; *Cent.* **1930**, II 3637; *C.A.* **25**, 710 (1931). (3) Böttcher (to I.G.), Ger. 487,787, Dec. 16, 1929, *Cent.* **1930**, I 1050.

3:7893 3-CHLOROPENTANONE-2 C_5H_9OCl Beil. I - 678
(α-Chloro-*n*-propyl methyl ketone) I_1—
I_2—



B.P. 130° (1)
130–133° (2)
63° at 95 mm. (3) cf. (7)
62–66° at 56 mm. (7)

[For prepn. of C̄ from pentanone-2 (methyl n-propyl ketone) (1:5415) with Cl_2 (yields: 35.5% (3), 85% crude (2)) cf. (6) or with SO_2Cl_2 in C_6H_6 (44% yield (7)) see indic. refs.; from ethyl α-chloro-α-ethylacetoacetate [Beil. III-694, III_1-(241), III_2-(438)] by ketonic cleavage with dil. HCl in s.t. at 180° for 4–6 hrs. see (1) cf. (7).]

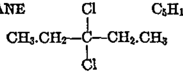
[C̄ in abs. alc. treated with NH_3 gas yields (2) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215–217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 2-chloropentanone-3 (3:7935) similarly treated gives same prod.) — C̄ with equiv. amt. ethyl β-aminocrotonate [Beil. III-654, III_1-(228), III_2-(423)] in pres. of excess conc. NH_4OH gives (27.3% yield (4)) ethyl 2,5-dimethyl-4-ethylpyrrolecarboxylate-3 [Beil. XXII-33, $XXII_1$-(501)], cryst. from dil. MeOH, m.p. 74–75° (4); note, however, m.p. 106–107° (5) reported for this prod. obtd. in a dif. way.]

[C̄ with thioformamide gives (29% yield (7)) 4-methyl-5-ethylthiazole, b.p. 169.5–170° at 745 mm., 78–79° at 25 mm. (7).]

3:7893 (1) Conrad, *Ann.* **186**, 241–242 (1877). (2) Démetre-Vladesco, *Bull. soc. chim.* (3) **6**, 832–834 (1891). (3) Korschun, *Bull. soc. chim.* (4) **3**, 595–596 (1908). (4) Korschun, *Bull. soc. chim.* (4) **3**, 594–595 (1908). (5) Vecchi, *Gazz. chim. ital.* **44**, I 477 (1914). (6) Justoni, *Chimica e industria (Italy)* **24**, 195–201 (1942); *Cent.* **1943**, I 1659. (7) Buchman, Richardson, *J. Am. Chem. Soc.* **67**, 397 (1945).

3:7895 3,3-DICHLOROPENTANE

$C_5H_{10}Cl_2$ — Beil. I — ; I_1— ; I_2-(96)



B.P. 131–132° at 750 mm. (1)
32° at 14 mm. (1)

$D^{20}_{-} = 1.053$ (1) **$n^{20}_{D} = 1.442$ (1)**

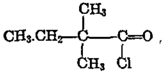
C̄ has never been reported in completely pure form; the above material contains abt. 20% 2,3-dichloropentane (3:8010) q.v. (1).

[For prepn of C̄ (together with other products) from diethyl ketone (1:5420) with PCl_5 see (1).]

3:7895 (1) Bourgeul, *Compt. rend.* **178**, 1559 (1924); *Bull. soc. chim.* (4) **35**, 1635 (1924); *Ann. chim.* (10) **3**, 371 (1925).

3:7900 α,α-DIMETHYL-n-BUTYRYL CHLORIDE
(Dimethyl-ethyl-acetyl chloride)

$C_6H_{11}OCl$ — Beil. II - 336 ; II_1— ; II_2—



B.P. 132°	**at 760 mm. (6)**	**$D^{20}_4 = 0.9801$ (1)**	**$n^{20}_D = 1.4245$ (5)**
131.8–132.4°	**at 748 mm. (1)**		
131.7–131.9°	**(2)**		
129.8°	**at 727 mm. (5)**	**$D^0_4 = 0.9973$ (1)**	
23°	**at 12 mm. (3)**		
27°	**at 11 mm. (4)**		

[For prepn. of C̄ from 2,2-dimethylbutanoic acid-1 (1:1113) with $SOCl_2$ (50% yield (5)) see (1) (5); with benzoyl chloride (yield not given) see (6).]

[For reactn. of C̄ with isobutyl zinc iodide yielding (3) 2,5,5-trimethylheptanone-4

(*tetrahydroartemisaketone*) see (3); for reactn. of C̄ with isopropyl MgBr yielding (by reducing actn.) 2,2-dimethylbutanol-1 (1:6204) and 2,4,4-trimethylhexanol-3 (5) see (5).]

C̄ on hydrolysis yields 2,2-dimethylbutanoic acid-1 (1:1113) q.v. (for the amide, anilide, *p*-toluidide, α-naphthalide, and other derivatives corresponding to C̄ see 1:1113).

3:7900 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243-250 (1933). (2) Kohlrausch, Pongratz, *Z physik. Chem* **B-22**, 383 (1933). (3) Ruzicka, Reichstein, Pulver, *Helv. Chim. Acta* **19**, 648-649 (1936). (4) Reichstein, Rosenberg, Eberhardt, *Helv. Chim. Acta* **18**, 723 (1935). (5) Whitmore, Foster, *J. Am. Chem. Soc.* **64**, 2966-2968 (1942). (6) Degnan, Shoemaker, *J. Am. Chem. Soc.* **68**, 104-105 (1946).

3:7903 CHLOROBENZENE  C_6H_5Cl **Beil. V - 199**
(Phenyl chloride) **V_1-(109)**
V_2-(148)

B.P.	F.P.	
132.10-132.12° cor. (1)	**−44.0°** (21) (22)	D_4^{25} = **1.1016** (14)
132.07° at 760 mm. (2)	**−45.0°** (23) (24)	**1.1012** (31)
132.02° at 761.8 mm. (3)	(7) (25)	**1.1011** (32)
132.0° at 760 mm. (4)	**−45.1°** (4)	**1.10091** (4)
(5) (6) (7) (8) (9) (10)	**−45.2°** (26) (27)	n_D^{25} = **1.5222** (14)
131.83° at 760 mm. (11)	(28) (29)	**1.5221** (28)
131.7° at 760 mm. (12)	(8)	**1.5217** (31)
131.6° (13)	**−45.29°** (2)	**1.5215** (36)
131.4-131.6° at 748 mm. (14)	See Note 2.	D_4^{20} = **1.1066** (38)
130.7° at 755 mm. (15)		**1.10643** (33)
130.5° at 755 mm. (16)		**1.1064** (12)
129.6° at 719 mm. (17)		**1.10631** (4)
114.9° at 468.5 mm. (17)		n_D^{20} = **1.5251** (37)
99.7° at 292.8 mm. (17)		**1.525** (2)
44.8° at 30 mm. (18)		**1.52479** (38)
See Note 1.		**1.52459** (15)
		D_4^{15} = **1.11172** (4)
		See Note 3.
		n_D^{15} = **1.52748** (4)
		1.5272 (39)
		See Note 4.

Note 1. For further data on b.p. of C̄ at various press. in range 98-758 mm. see (19), between 3-11, 188 mm., see (20)

Note 2. For details on m.p. of C̄ under high pressures see (26) (30).

Note 3. For details on D_4^t over range 0 3-123.6° see (34), over range −42.7° to + 126° see (35).

Note 4. For details of change of refractive index with pressure see (40)

C̄ is pract. insol. aq.; for precise data see (11) (225). — C̄ is very eas. sol. alc , ether, C_6H_6, $CHCl_3$, CS_2. — For detn. of C̄ in mixt. with C_6H_6 and the dichlorobenzenes see (226) (227). — *For use of C̄ as immersion fluid in refractometry see* (228). — For toxicity of C̄ see (229). — For brief study of detn. of vapors of C̄ in air using a combustion method see (230).

Selected data and references on physical properties of mixts. of C̄ with other cpds (for additional data and references on many other systems see Beilstein).

Binary systems. C̄ with H_2O forms a const -boilg. mixt , b.p. 90.2° at 760 mm., contg; 71.6° C̄ (41) (use in sepn of C̄ from polychlorobenzenes see (69)): C̄ with *acetone* (1:5400).

[illegible] $\bar{C}$ with acetic acid (1:1010) [illegible]

[illegible]

nitrobenzene, f.p./compn. data + diagram (eutectic, m.p. −50.7° contg. 78.3 wt. % $\bar{C}$) see (21): $\bar{C}$ with *pyridine*, f.p./compn. data + diagram (eutectic, m.p. −63.5°, contg. 54% $\bar{C}$) and also n_D^{25}/compn. diag. see (28): $\bar{C}$ with *o-chlorotoluene* (3:8245), f.p./compn. diagram (eutectic, m.p. abt. −71°, contg. 39.4 mole % $\bar{C}$) see (44); $\bar{C}$ with *m-dichlorobenzene* (3:5960), f.p./compn. data, see (23): $\bar{C}$ with *benzoyl chloride* (3:6240), f.p./compn. data see (45): $\bar{C}$ + *ethylene dibromide*, f.p./compn. diag. (eutectic, m.p. −55° contg. 83 mole % $\bar{C}$) see (44); vapor-press. equil. see (46): $\bar{C}$ + *bromobenzene*, f.p./compn. diagram (no eutectic) see (22) (24); for use in testing efficiency of distillation columns see (39): $\bar{C}$ + *iodobenzene*, f.p./compn. diagram (eutectic, m.p. −51.5°, contg. 57% $\bar{C}$) see (22) (24): $\bar{C}$ with *fluorobenzene*, f.p./compn. diagram (complex system) see (22) (24).

Ternary Systems. $\bar{C}$ with *aq.* + HCl forms ternary const.-boilg. mixt., b.p. 96.6° at 756 mm., contg. 74.5 wt. % $\bar{C}$ + 20.2 wt. % aq. + 5.3 wt. % HCl (41): $\bar{C}$ with *aq.* + *acetone*, solubility diagram see (47): $\bar{C}$ + *ethylene glycol* (1:6465) + *acetone*, soly. of system at 23° see (48).

Preparation of $\bar{C}$. Because of the magnitude of the literature on this topic only a few selected references can be given here; reference should also be made to Beil. V-199, V_1-(109) and V_2-(148).

[For prepn. of $\bar{C}$ from C_6H_6 with Cl_2 in pres. of $SnCl_4$ at 30–40° (49), with NOCl at 425° (50), with HCl + O_2 (air) + cat. (51) see indic. refs.; for discussion of prepn. of industrial $\bar{C}$ see (52); for study of photochem. chlorination of C_6H_6 see (53).]

[For prepn. of $\bar{C}$ from aniline via formn. of benzenediazonium chloride/$ZnCl_2$ cpd. and htg. with molten phenol (40% yield $\bar{C}$ + 26% hydroxybiphenyl + 20% diphenyl ether (54)) or by isolation of solid benzene diazonium chloride and cautious decompn. by warming in various org. solvents see (55); from *p*-chloroaniline via formn. of *p*-chlorobenzenediazonium chloride/$ZnCl_2$ cpd. and htg. latter with EtOH (67% yield) or EtOH + Zn dust (60% yield) see (54); from phenylhydrazine by oxidn. with aq. $FeCl_3$ at 70° (61% yield) or with $HClO_3$ (30% yield) see (56); fro[illegible] (60% yield (57)), sulfuryl chloride (57), [illegible] (57)), other aromatic sulfonyl chlorides [illegible] amines (59), or *N*-chloro-*p*-chlorobenzaldimine (60), see indic. refs.]

[For formn. of $\bar{C}$ from benzoyl chloride (3:6240) on htg. in porcelain tube at 550–600° see (61); from benzeneazotriphenylmethane on warming in CCl_4 see (62); from *bis*-(*p*-chlorophenyl)zinc by reaction with aq. see (63); from phenylboric acid with Cl_2/aq. or refluxed with aq. $CuCl_2$ (85% yield) see (64); from C_6H_6 + *n*-butyl chlorosulfonate + $AlCl_3$ (11% yield) see (65); from C_6H_6 with $SeCl_4$ + $AlCl_3$ see (66); from 4-chlorodiphenyl sulfide by htg. with sulfur see (67); from 2-chlorobenzophenone (3:0715) or 4-chlorobenzophenone (3:1914) on fusion with KOH/NaOH see (68).]

Pyrolysis. $\bar{C}$ passed over Pt wire at bright red heat (70) or through hot Fe tube (71) yields 4,4′-dichlorobiphenyl (3:4300) accompanied by biphenyl (1:7175), 4-chlorobiphenyl (3:1912), and other products.

Reduction. $\bar{C}$ in EtOH at 55° with excess H_2 at 3 atm. in pres. of Adams' cat. readily (72) yields cyclohexane (1:8405). — $\bar{C}$ with H_2 or $NH_2.NH_2$ in MeOH or EtOH in pres. of $Pd/CaCO_3$ gives (73) cf. (74) small yields of biphenyl (1:7175). — $\bar{C}$ with Na in boilg. EtOH (75), or Na/Hg in EtOH (76), or Na in AmOH (77), or NaOAm in AmOH (78) is dehalogenated, but extent of reactn. varies with conditions. — $\bar{C}$ with HI + P is unaffected at 300° but at 375° yields (79) benzene. — $\bar{C}$ in aq. or dil. alc. alk. with H_2 in pres. of Ni

splits off all (80) its halogen as HCl. — $\bar{C}$ with H_2 + Ni at 270° yields (81) benzene + biphenyl.

Behavior with chlorine. $\bar{C}$ with Cl_2 may add or substitute or both according to conditions. — $\bar{C}$ under dil. aq. NaOH with excess Cl_2 in sunlight (82) or with Cl_2 at 0° in dark as directed (83) (84) gives (90% yield (83)) heptachlorocyclohexane [Beil. V-23, V_2-(12)] (known in 2 stereoisomeric forms, "α," m.p. 146° (82), "β," m.p. 260° (82)). [For study of relative amts. addition and substitution with $\bar{C}$ + Cl_2 see (85).]

$\bar{C}$ with Cl_2 in pres. of $AlCl_3$ (86), Al/Hg (87), or $FeCl_3$ (86), or $\bar{C}$ with SO_2Cl_2 + S_2Cl_2 + $AlCl_3$ (88), or $\bar{C}$ htd. with $FeCl_3$ (89) or $PbCl_4{\cdot}2NH_4Cl$ (90), gives mainly 1,4-dichlorobenzene (3:0980) accompanied by other products. — $\bar{C}$ with Cl_2 at 400–700° in pres. of cat. yields (91) (92) 1,3-dichlorobenzene (3:5960) + 1,3,5-trichlorobenzene (3:1400) and other products.

Behavior with bromine. $\bar{C}$ with Br_2 (93) under aq. (82) or in pres. of $AlCl_3$ (94), Al/Hg (95), Al (99), or Fe (99), or $\bar{C}$ htd. with $FeBr_3$ (96), gives mainly 4-bromochlorobenzene [Beil. V-209, V_1-(116), V_2-(162)], m.p. 66°, together with other products; for study of rate in AcOH see (97). — $\bar{C}$ with Br_2 at elevated temp. gives greatly increased proportion of *meta*-bromochlorobenzene; e.g., $\bar{C}$ with Br_2 at 475° gives (98) 53% *m*-, 27% *p*-, and 20% *o*-bromochlorobenzenes.

Behavior with metals. $\bar{C}$ with Li in dry ether under dry N_2 gives (35–49% yield (100)) phenyllithium [Beil. XVI_1-(589)]; for reactns. of latter with fluoro, chloro, bromo, or iodobenzene see (101).

$\bar{C}$ on boilg. with Na yields (102) C_6H_6, biphenyl, and other products; $\bar{C}$ with Na in boilg. toluene yields mainly (102) C_6H_6 together with other prods. — $\bar{C}$ with amylsodium (from amyl chloride + Na) in lgr. gives (103) (104) (105) phenylsodium [Beil. XVI_1-(589)] which with CO_2 gives (105) benzoic acid; $\bar{C}$ with Na + diethyl carbonate in C_6H_6 gives (79% yield (106)) (for use of other esters such as methyl benzoate, ethyl benzoate, or diethyl oxalate in ether see (107)) or $\bar{C}$ with Na + benzophenone in C_6H_6 gives (98% yield (106)) (108) triphenylcarbinol (1:5985). — $\bar{C}$ with Na + $AsCl_3$ in xylene gives (82% yield (109)) triphenylarsine, $\bar{C}$ with Na + $SbCl_3$ in xylene yields (109) triphenylstibine.

$\bar{C}$ with Mg/Cu alloy in pres. of I_2 (110), or $\bar{C}$ with Mg in s.t. at 150–160° for 3 hrs. (111) (112), or $\bar{C}$ refluxed with Mg + Cu_2Cl_2 (113), gives (yields. 80% (110), 85% (111)) phenyl magnesium chloride.

Behavior with Al halides. $\bar{C}$ does not react with $AlCl_3$ even on long boilg. (dif. from bromobenzene and iodobenzene which react at once) (114). — $\bar{C}$ with freshly prepared fused $AlBr_3$ yields (115) bromobenzene.

Behavior with $AlCl_3$ + other compounds. $\bar{C}$ (2 moles) with CCl_4 (1 mole) + $AlCl_3$ (1.75 moles) in CS_2 gives (116) (117) *bis*-(4-chlorophenyl)dichloromethane [Beil. V-592], m.p. 52–53°, together with other products; $\bar{C}$ (6 moles) with CCl_4 (1 mole) + $AlCl_3$ (1 mole) htd. at 60–70° gives mainly (118) 2-chlorophenyl-*bis*-(4-chlorophenyl)chloromethane [Beil. V-703], m.p. 153°, accompanied by a small amt. *tris*-(4-chlorophenyl)chloromethane [Beil. V-703], m.p. 113°.

$\bar{C}$ with AcCl (3:7065) or Ac_2O + $AlCl_3$ yields *p*-chloroacetophenone (3:6735) q.v. for details.

$\bar{C}$ + furoic acid (1:0475) + $AlCl_3$ gives (18% yield (119)) 6-chloronaphthoic acid-1 (3:4845); $\bar{C}$ + methyl furoate (1:3452) + $AlCl_3$ gives in good yield (120) methyl 6-chloro-1-naphthoate.

$\bar{C}$ with phthalic anhydride (1:0725) + $AlCl_3$ gives (121) (122) (123) (124) *o*-(4-chlorobenzoyl)benzoic acid [Beil. X-750, X_1-(356)], m.p. 147–148°, which on ring closure with

conc. H_2SO_4 yields 2-chloroanthraquinone (3:4922) q.v. [For corresp. reactns. of C̄ with 4-bromophthalic anhydride (125), 4-sulfophthalic anhydride (126), naphthalene-1,2-dicarboxylic acid anhydride (127), or naphthalene-2,3-dicarboxylic acid anhydride (128) see indic. refs.]

Miscellaneous condensations. C̄ with acetylene + $AlCl_3$ gives (129) 1,2-bis(4-chlorophenyl)ethane (4,4'-dichlorodibenzyl) + other prods., cf. also (130). — C̄ with propylene in pres. of sulfonic acids at 86–130° gives (131) isopropylbenzene (cumene) (1:7440). — C̄ + hexene-3 + H_2F_2 gives (25% yield (132)) 4-chloro-(1'-ethylbutyl)benzene. — C̄ + cyclohexene + conc. H_2SO_4 gives (50% yield (133)) 4-chlorophenylcyclohexane. — C̄ + allyl chloride (3:7035) + conc. H_2SO_4 gives (133) 1-chloro-2-(*p*-chlorophenyl)propane.

C̄ + isopropyl alc. with 80% H_2SO_4 at 70° gives (72% yield (134)) 4-chloro-isopropylbenzene (3:8705). — C̄ with *ter*-butyl alc. + $AlCl_3$ gives (135) 4-chloro-*ter*-butylbenzene; C̄ with *ter*-amyl alc. + $AlCl_3$ gives (135) 4-chloro-*ter*-amylbenzene.

C̄ + CO + $AlCl_3$ + $TiCl_4$ at 60 atm. and 30–35° (136) or C̄ + HCN + $AlCl_3$ at 100° for 6 hrs. (137) gives *p*-chlorobenzaldehyde (3:0765). — C̄ + CO + cat. + steam at 300–400° (138) (139) gives benzoic acid. — C̄ with paraformaldehyde + $ZnCl_2$ (140) (142) or C̄ with formalin + HCl (141) or C̄ with chloromethyl methyl ether (3:7085) + $ZnCl_2$ (142) or C̄ with *bis*-(chloromethyl) ether (3:5245) + $ZnCl_2$ (142) yields *p*-chlorobenzyl chloride (3:0220) q.v. — C̄ with *p*-chlorobenzyl chloride (3:0220) + H_2SO_4 yields (142) 4,4'-dichlorodiphenylmethane.

C̄ with chloral (3:5210) or chloral hydrate (3:1270) + conc. or fumg. H_2SO_4 gives 1,1,1-trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT") (3:3298) q.v.

Hydrolysis. C̄ is unaffected by protracted boilg. with aq. or even alc. alk.; however, by use of increased temp. and press. especially in pres. of catalysts the hydrolysis of C̄ constitutes an extremely important industrial process for manufacture of phenol.

For general studies on the catalytic hydrolysis of C̄ to phenol with steam at elevated temperatures see (143) (144) (145) (146); for patents employing this method see (147)–(159) incl. — For résumé of prepn. of phenol via Raschig method (C_6H_6 + HCl + O_2 to C̄ with subsequent hydrolysis) see (160); for relevant patents see (161) (162) (163). — For sepn. of products of hydrolysis see (41) (164).

C̄ may also be hydrolyzed to phenol by means of aq. NaOH, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, etc., at elevated temp. and press. especially in pres. of catalysts, notably copper: for impt. general review of these methods up to 1927 see (165); for general discussion see (166); for recent patents on this process and its variants see (167)–(182) incl. — For conv. of C̄ with alk. to 4-hydroxybiphenyl (1:1585) see (183) or to diphenyl ether (1:7125) see (184) (185) (186).

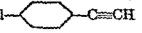
C̄ htd. with aq. Na_2S, NaSH, or H_2S under press. gives (187) (188) (189) (190) diphenyl sulfide and/or thiophenol. — C̄ + H_2S + cat. at 700° gives (191) thiophenol.

[For use of C̄ in prepn. of sulfur dyes by htg. with sulfur see (192) (193).]

Ammonolysis. C̄ with dry NH_3 does not react even in pres. of Cu + I_2 and high temp. and press. (194). — However, C̄ with conc. aq. NH_4OH htd. at high temp. and press. especially in pres. of Cu, Cu cpds., or other cat. yields aniline and/or diphenylamine; for general discussion of this reactn. see (195) (196) (197) (198) (199); for illustrative patents see (200)–(208) incl.; for purification of reactn. prod. see (209) (210). — For behavior of C̄ with Na in liq. NH_3 (211) and its use in detn. of halogen content of C̄ (212) see indic. refs. — For behavior of C̄ with KNH_2 in liq. NH_3 see (213) (214).

Nitration. C̄ on mononitration, e.g., with mixt. of 10 ml. HNO_3 (D = 1.52) + 50 ml. HNO_3 (D = 1.48) for 25 g. C̄ at 0° (215), gives a prod. contg. 69.9% *p*-chloronitrobenzene [Beil. V-243, V_1-(130), V_2-(183)], m.p. 82°, together with 29.8% *o*-chloronitrobenzene [Beil. V-241, V_1-(129), V_2-(180)], m.p. 32°; the *p/o* ratio is but little different at −30°;

3:0590 *p*-CHLOROPHENYLACETYLENE C_8H_5Cl Beil. S.N. 474



M.P. 45.4–46.1° (1)
43.5–44° (2)

[For prepn. of $\bar{C}$ from *p*-chloro-α-chlorostyrene by elimination of HCl with 25% alc. KOH (36% yield (1)) (2) see indic. refs.]

[For study of dipole moment see (3).]

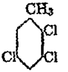
[$\bar{C}$ with I_2 in liq. NH_3 at −34° readily gives (98% yield (1)) *p*-chlorophenyl-iodo-acetylene, m.p. 84.7–85.0° (1).]

[$\bar{C}$ with NH_3/Cu_2Cl_2 as directed gives (50% yield (5)) di-(*p*-chlorophenyl)biacetylene, m.p. 258° (5).]

Ⓓ Di-(*p*-chlorophenylethynyl)mercury: m.p. 221–222° (2), 221.5° (1). [From $\bar{C}$ in alc with alk. K_2HgI_4 according to (4); *note that m.p. of this prod. is only slightly* higher than that (213–214°) for the corresp. prod. from *o*-chlorophenylacetylene (3:9497).]

3:0590 (1) Vaughn, Nieuwland, *J. Am. Chem. Soc.* **56**, 1207–1209 (1934). (2) Otto, *J. Am. Chem. Soc.* **56**, 1393–1394 (1934). (3) Otto, Wenzke, *J. Am. Chem. Soc.* **56**, 1314–1315 (1934). (4) Johnson, McEwen, *J. Am. Chem. Soc* **48**, 471 (1926). (5) Zal'kind, Fundyler, *J. Gen. Chem. (U.S.S.R.)* **9**, 1725–1728 (1939); *C.A.* **34**, 3719 (1940).

3:0610 2,3,5-TRICHLOROTOLUENE $C_7H_5Cl_3$ Beil. V - 299
V_1—
V_2—



M.P. 45–46° (1) B.P. 229–231° at 757 mm. (1)

[For prepn. of $\bar{C}$ from 3,5-dichloro-2-aminotoluene [Beil. XII-837] or from 2,5-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of $CuCl_2$ reactn. see (1); for formn. of $\bar{C}$ *from 3,5-dichlorotoluene (3:6310) with Cl_2 in pres. of Al/Hg see (2).*]

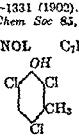
[$\bar{C}$ with Cl_2 in pres. of Al/Hg yields (3) 2,3,5,6-tetrachlorotoluene (3:2575).]

$\bar{C}$ on mononitration with cold fumg. HNO_3 (1) yields 2,3,5-trichloro-4(or 6)-nitrotoluene [Beil. V-333], ndls. from alc. or AcOH, m p 58–59° (1); $\bar{C}$ on dinitration with 6 pts. fumg. HNO_3 + 4 pts. conc. H_2SO_4 *yields 2,3,5-trichloro-4,6-dinitrotoluene [Beil. V-345]*, ndls. from alc. + AcOH, m p. 149–150° (1).

$\bar{C}$ on oxidn. with dil. HNO_3 in a s.t. at 140° yields *(1) 2,3,5-*trichlorobenzoic acid (3:4485), m.p. 162° (1).

3:0610 (1) Cohen, Dakin, *J. Chem Soc.* **81**, 1329–1331 (1902). (2) Cohen, Dakin, *J. Chem. Soc.* **81**, 1343–1344 (1902). (3) Cohen, Dakin, *J Chem Soc* **85**, 1284 (1904).

3:0618 2,4,6-TRICHLORO-3-METHYLPHENOL $C_7H_5OCl_3$ Beil. VI —
(2,4,6-Trichloro-m-cresol) VI_1- (189)
VI_2- (356)



M.P. 46° (1) (2) B.P. 265° (2)
45° (3) 162–163° at 28 mm. (3)

[For prepn. of $\bar{C}$ *from m-cresol (1:1730) in aq. alk. with excess Cl_2 (3) or from m-cresol* with Cl_2 in the dark (2) see indic. refs. (note that *m*-cresol with Cl_2 in sunlight yields (2)

3:7917 ***d,l*-2-CHLOROPROPANOL-1** (Propylene β-chlorohydrin; β-chloro-*n*-propyl alcohol)

$CH_3—CH(Cl)—CH_2(OH)$ C_3H_7OCl Beil. I - 356, I_1-(180), I_2-(369)

B.P. 133–134° cor.	at 762 mm. (1)	$D_{-}^{20} = 1.103$ (1)	$n_D^{20} = 1.43623$ (1)
133–134°	at 761 mm. (2)		
133–134°	at 760 mm. (3)	$D_4^{15} = 1.4505$ (9)	$n_D^{15} = 1.4766$ (9)
133°	(10)		
94°	at 8 mm. (9)		

[*See also* 1-*chloropropanol*-2 (3:7747).]

[For prepn. of C̄ from its acetate (see below) by alcoholysis with excess boilg. dry MeOH for 8 hrs. (83% yield) see (1); note that this prepn. really starts from the isomeric 1-chloropropanol-2, the conversion of which to C̄ involves the following steps: reaction with KOAc yielding $CH_3.CH(OH).CH_2(OAc)$, conversion of latter with HCl + $ZnCl_2$ to $CH_3.CH(Cl).CH_2(OAc)$, and finally alcoholysis to C̄ as mentioned above (1) (4); for formn. of C̄ by alk. hydrol. of its trichloroacetate see (9).]

[Note that although C̄ is formed in other ways (e.g., from propanediol-1,2 (propylene glycol) (1:6455) with HCl or S_2Cl_2 (5), from 2,3-epoxybutane (propylene oxide) (1:6115) *by addn. of* HCl (5), *from propylene with* HOCl (5), *or from α-chloro-n-propylamine with* HNO_2 (6)) the product of these reactions appears to be (5) (6) an inseparable mixt. of about 40% C̄ with 60% of the isomeric 1-chloropropanol-2 (3:7747).]

Reactions of the halogen atom of C̄. [C̄ when added dropwise to conc. aq. KOH loses HCl yielding (1) 2,3-epoxybutane (propylene oxide) (1:6115), b.p. 35°. — C̄ with KCN in 80% alc. contg. some NaI gives on warming (60% yield (2)) β-hydroxy-*n*-butyronitrile [Beil. III-309, III_2-(221)], b.p. 214–215° (2); note that this is *not* the product to be expected from simple replacement of Cl by CN and apparently results from preliminary formation of propylene oxide to which HCN then adds so as to give a straight (rather than forked) carbon chain.]

Reactions of the OH group of C̄. [C̄ reacts normally as a substituted primary alc. giving ethers, esters, oxidn. products, etc.]

[C̄ readily gives the corresp. ethers; e.g., C̄ with Me_2SO_4 on warming gives (7) β-chloro-*n*-propyl methyl ether, b.p. 98–99° at 756 mm., $D_4^{20} = 0.9946$, $n_D^{20} = 1.40754$ (7); C̄ with EtOH + conc. H_2SO_4 on htg. gives (54% yield (7)) β-chloro-*n*-propyl ethyl ether, b.p. 116–117° at 758 mm., $D_4^{20} = 0.9828$, $n_D^{20} = 1.41285$ (7); for corresp. formn. of ethers with *n*-propyl alc. (1:6150) and with allyl alc. (1:6145) see (7).]

[C̄ (1 mole) with SO_2Cl_2 (2.5 moles) at 130° gives (16% yield (7)) *bis*-(β-chloro-*n*-propyl) ether, b.p. 188° at 762 mm., $D_4^{20} = 1.109$, $n_D^{20} = 1.4467$ (7); note that this ether is not obtd. from C̄ with conc. H_2SO_4 (7).]

[C̄ on oxidn. with 3 wt. pts. conc. HNO_3 as directed (8) (2) gives (85% yield (2)) α-chloropropionic acid (3:6125), accompanied by some acetic acid (1:1010) and oxalic acid (1:0445); note that C̄ on oxidn. with chromic acid yields no α-chloropropionic acid but only acetic acid (1:1010) and formic acid (1:1005) (2).]

—— **β-Chloro-*n*-propyl acetate** [Beil. II-129, II_1-(58), II_2-(139)]: oil, insol. aq., b.p. 151–152° at 768 mm. (11), 152–153° at 750 mm. (1). [Prepd. indirectly; furthermore the prods. reported may be contaminated with some of the isomeric β-chloroisopropyl acetate cf. (10).]

—— **β-Chloro-*n*-propyl benzoate**: unreported.

—— **β-Chloro-*n*-propyl *p*-nitrobenzoate**: unreported.

—— **β-Chloro-*n*-propyl 3,5-dinitrobenzoate**: unreported.

for f.p./compn curve of system *p*-chloronitrobenzene/*o*-chloronitrobenzene (eutectic, m p. 14.7°, contg. 33.1% *p*-isomer) see (215). — For mononitration using 0.9 g. of 70% HNO_3 + 1.29 g. 94% H_2SO_4 per gram of $\bar{C}$ (216) or using nitrosulfonic acid (from fumg. HNO_3 treated with SO_2) at 30° (217) or using $Fe(NO_3)_3$ in Ac_2O at 40–45° (218) see indic. refs. — Note that no appreciable amt. of *m*-chloronitrobenzene is formed by direct nitration of $\bar{C}$.

$\bar{C}$ on dinitration, e.g., with 5 wt. pts. of a mixt. consisting of equal wts. of 92.8% HNO_3, 93.3% H_2SO_4, and fumg H_2SO_4 (contg. 14.2% SO_3) at 95° for 2 hrs. (219) gives 96.7% yield 2,4-dinitrochlorobenzene [Beil V-263, V-(137), V_2-(196)], cryst. from alc., m.p. 52–53°. [The other dinitro isomers are known but need not be discussed here.]

Sulfonation. $\bar{C}$ is insol. in cold conc. H_2SO_4; however, $\bar{C}$ on warming or on stdg. at room temp. for 48 hrs. (220) with equal wt. conc. H_2SO_4 dissolves and later ppts. *p*-chlorobenzenesulfonic acid [Beil. XI-54, XI_1-(14)], anhydrous cryst. from $CHCl_3$, m.p. 92–93° (220), monohydrate from aq , m.p. 67° (221). — $\bar{C}$ with fumg. H_2SO_4 (10% SO_3) below 60° for 1 hr. then poured into 6 vols. satd. aq. NaCl soln. gives (222) (223) sodium salt of *p*-chlorobenzenesulfonic acid which with PCl_5 yields corresp. sulfonyl chloride (see below). — For reactn. of $\bar{C}$ with $ClSO_3H$ see below. — [The corresp. *bis*- (4-chlorophenyl) sulfone [Beil. VI-327, VI_1-(149)] which may be formed in small amt. has m.p. 147–148°.] [For study of kinetics of sulfonation of $\bar{C}$ see (231).]

Ⓓ ***p*-Bromochlorobenzene:** $\bar{C}$ with 0.25–0.50 mole Br_2 at 60° in pres. of Fe gives (88% yield (99)) *p*-bromochlorobenzene, cryst. from alc., m.p. 67–68°.

Ⓓ **2,4-Dinitrochlorobenzene:** $\bar{C}$ on htg. with mixt. of HNO_3 + H_2SO_4 (see above under nitration) at 95° for 2 hrs. gives (96.7% yield (219)) 2,4-dinitrochlorobenzene, cryst. from alc., m p. 52–53°.

Ⓓ **4-Chlorobenzenesulfonamide:** $\bar{C}$ with $ClSO_3H$ in $CHCl_3$ as directed (224) gives 4-chlorobenzenesulfonyl chloride, cryst. from dry ether, m.p. 53°, which by boilg. with conc. NH_4OH or htg. with solid $(NH_4)_2CO_3$ for 30 min. at 100° gives 4-chlorobenzenesulfonamide, cryst. from dil. alc., m.p. 142–143° u.c. (224).

3:7903 (1) Brooks, Hobbs, *J. Am. Chem. Soc.* **62**, 2851 (1940) (2) Stull, *J. Am. Chem. Soc.* **59**, 2729 (1937). (3) Feitler, *Z. physik. Chem.* **4**, 68 (1889). (4) Timmermans, Martin, *J. chim. phys.* **23**, 780–782 (1926). (5) Lecat, *Rec. trav. chim.* **46**, 242 (1927). (6) Grimm, Patrick, *J. Am Chem. Soc.* **45**, 2799 (1923). (7) [illegible] 921). (8) Timmermans, van der Horst, Onnes, *Co* [illegible] 377. (9) Young, *Proc. Roy. Dublin Soc.* **12**, 424 (1 [illegible] *Belg.* **24**, 244–269 (1909), *Cent.* **1910**, II 442.

(11) Gross, Saylor, *J. Am. Chem Soc.* **53**, 1748 (1931). (12) Matthews, *J. Am. Chem. Soc* [illegible], 619 (1943). (14) Thomson, *J. Chem. Soc.* [illegible] 3, 56 (1935). (16) Hurdis, Smyth, *J. Am.* [illegible] *Z. physik Chem.* **44**, 362–363 (1903). (18) [illegible] (19) Ramsay, Young, *Z physik. Chem.* **1**, [illegible] (1889).

(21) Hrynakowski, Szmyt, *Z physik. Chem.* **A-182**, 110–112 (1938). (22) Pascal, *Bull. soc. chim.* (4) **13**, 745–752 (1913). (23) Timmermans, *Bull soc chim. Belg.* **43**, 633 (1934). (24) L. Klemm, W. Klemm, G. Schiemann, *Z physik. Chem.* **A-165**, 384–386 (1933). (25) Timmermans, *Bull. soc. chim Belg.* **25**, 300–327 (1911); *Cent* **1911**, II 1015. (26) Bridgman, *J. Chem. Phys.* **9**, 794–795 (1941). (27) Skau, *J Phys Chem.* **37**, 612–613 (1933). (28) Burnham, Madgin, *J. Chem. Soc.* **1936**, 790–792. (29) Menschutkin, *J. Russ Phys.-Chem. Soc* **43**, 402 [illegible] (33) [illegible] ius, *Z.* [illegible] (36) [illegible] ulewa, [illegible] 1879).

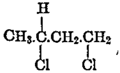
from dextrorotatory amyl chloride by photochemical chlorination with SO_2Cl_2 in pres. of benzoyl peroxide see (4).]

$\bar{C}$ *on boilg. with aq.* K_2CO_3 *gives* (1) *(together with other products)* 1-chloro-2-methylbutene-1 (3:7303), b p. 96–97°.

$\bar{C}$ on oxidn. with $KMnO_4$ gives (2) butanone-2 (ethyl methyl ketone) (1:5405).

3:7920 (1) Chalmers, *Trans. Roy. Soc. Can.* (3) **22**, III 69–78 (1928). (2) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) 8, 1062–1067 (1938); *Cent.* **1939**, II 4221; *C.A.* **33**, 3755 (1939). (3) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) 8, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939). (4) Brown, Kharasch, Chao, *J. Am. Chem. Soc.* **62**, 3437–3439 (1940).

3:7925 1,3-DICHLOROBUTANE $C_4H_8Cl_2$ Beil. I —
I_1-(38)
I_2—



B.P. 134° (1) D_4^{20} = **1.1158** (3) n_D^{20} = **1.445**
131–133° at 758 mm. (3)

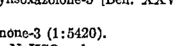
[For prepn. *from butanediol-1,3 by htg. in s.t. with conc. HCl (satd. at 0°) see* (1); for prepn. from 1-chlorobutane (*n*-butyl chloride) (3:7160) by actn. of Cl_2 in light (other products also being formed) see (2) (3) (4) (5); for prepn. from 2-chlorobutane (3:7125) by actn. of Cl_2 see (6).]

$\bar{C}$ on passing over alkali (NaOH, K_2CO_3, soda-lime, etc.) at elevated temperatures (e.g., 700–750°) yields butadiene-1,3. [For studies of this reaction see (2) (4) (5).]

$\bar{C}$ is readily saponified with aq. K_2CO_3 to butanediol-1,3 (1:6482) (6).

3:7925 (1) Fargher, Perkin, *J. Chem. Soc.* **105**, 1356 (1914). (2) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4050–4052 (1930). (3) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) 7, 893–896 (1937); *Cent* **1938**, II 2575; *C.A.* **31**, 5755 (1937). (4) Carothers (to du Pont), U.S. 2,038,593, U.S. 2,070,- Churbakov,

3:7935 2-CHLOROPENTANONE-3 C_5H_9OCl Beil. I - 681
(α-Chloroethyl ethyl ketone; α-chlorodiethyl ketone) I_1—
I_2—



B.P. 135° (1) (2)
145° (3)

Oil, insol. aq., sol. alc., ether.

[For prepn. of $\bar{C}$ from pentanone-3 (diethyl ketone) (1:5420) with Cl_2 (3) (4), with Cl_2 in pres. of aq. + $CaCO_3$ (86% yield (1)), or with Cl_2 in vapor-phase chlorination (4) see indic. refs.; from 4-chloro-4-methyl-3-ethylisoxazolone-5 [Beil. XXVII-163] with hydrochloric acid see (2).]

$\bar{C}$ on reduction with H_2 yields (3) pentanone-3 (1:5420).

$\bar{C}$ does *not* (3) form a cpd. with satd. aq. $NaHSO_3$ soln.

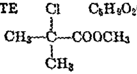
$\bar{C}$ dis. readily in aq. alk. yielding a soln. (presumably contg. pentanone-3-ol-2) which readily reduces $NH_4OH/AgNO_3$ and reduces Fehling's soln. on warming (3).

[$\bar{C}$ in abs. alc. treated with NH_3 gas yields (3) 2,5-dimethyl-3,6-diethylpyrazine [Beil. XXIII-101], liq., b.p. 215–217°, forming with aq. a sublimable hydrate, m.p. 42.5°. (Note that 3-chloropentanone-2 (3:7893) similarly treated gives the same prod.)]

—— 2-(Phthalimido)propanol-1 (*N*-(β-hydroxyisopropyl)phthalimide): lfts. from EtOAc m.p. 99–101° (10). [Prepd. indirectly (10); note that the prod. obtd. (10) from C̄ with K phthalimide in s.t. at 200–230° was the isomeric 1-(phthalimido)propanol-2, m.p. 88–89° (10), but whether this result was due to contamination of C̄ with the isomeric 1-chloro-propanol-2 (3:7747) or the rearr. has never been clarified.]

3:7917 (1) Henry, *Rec. trav. chim.* **22**, 327–333 (1903). (2) Dewael, *Rec trav. chim.* **33**, 504–507 (1924) (3) Henry, *Rec. trav. chim.* **22**, 209–210 (1903). (4) Henry, *Bull. acad. roy. Belg.* **1902**, 445–494; *Cent.* **1903**, II 929. (5) Smith, *Z. physik Chem.* **93**, 59–85 (1919). (6) Smith, Platon, *Ber.* **55**, 3150–3155 (1922). (7) Dewael, *Bull soc. chim. Belg.* **34**, 343–346 (1925). (8) Henry, *Rec. trav chim* **22**, 341–344 (1903). (9) Gayler, Waddle, *J. Am. Chem. Soc.* **63**, 3359 (1941). (10) Gabriel, Ohle, *Ber.* **50**, 807, 812 (1917).
(11) Dewael, *Bull. soc. chim. Belg* **39**, 400 (1930).

3:7918 METHYL α-CHLOROISOBUTYRATE $C_5H_9O_2Cl$ Beil. S.N. 162



B.P. 135°	at 760 mm. (7)	D_{15}^{15} = 1.0893 (3)		n_D^{21} = 1.4122	(7)
133–135°	at 760 mm. (1) (2)				
128–129.5°	at 753 mm. (3)			n_D^{15} = 1.4019	(3)
64–65°	at 55 mm. (3)				
42–44°	at 17 mm. (7)				

[For prepn of C̄ from α-chloroisobutyric acid (3:0235) with MeOH see (3) (4); for formn. of C̄ as by-product of reactn. of methyl α-hydroxyisobutyrate (1:3206) with phosgene (3:5000) + pyridine see (1) (2) (6).]

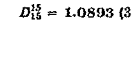
[C̄ on htg. at 500–510° (1), or passed over silica gel at 300° (4), or htd. with anhydrous $FeCl_3$ for 4 hrs. at 100° (5), or htd. with quinoline in pres. of hydroquinone (3), gives (83% yield (5)) methyl methacrylate, b.p. 100–101°.]

3:7918 (1) Burns, Jones, Ritchie, *J Chem. Soc.* **1935**, 717. (2) Ritchie, *J. Chem. Soc.* **1935**, 1059. (3) Zal'kind, Markov, *J Applied Chem. (U.S.S R)* **10**, 1042–1044 (1937), *Cent.* **1938**, II 2421; *C.A* **32**, 1652 (1938). (4) du Pont Co. & Loder, Brit 428,223, June 6, 1935, *Cent.* **1936**, I 179; *C A.* **29**, 6607 (1935). (5) Barrett (to du Pont Co.), U S 2,013,648, Sept 10, 1935; *Cent.* **1936**, I 3217, *C A.* **29**, 6902 (1935) (6) Imperial Chem Ind & Ritchie, Jones, Burns, Brit 424,885, March 4, 1935, *Cent.* **1936**, I 2440, *C.A* **29**, 5124 (1935). (7) Kahovec, Kohlrausch, *Monatsh.* **74**, 116 (1943).

3:7920 *d,l*-1,2-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I —

I_1—

I_2-(101)



B.P. 133–135°	(1)	D_4^{20} = 1.0785 (1)	$n_D^{23.6}$ = 1.4432 (4)
133.5° at 760 mm. (calcd.)	(4)	1.0766 (4)	
71.5° at 100 mm.	(4)		

[For prepn. of C̄ from 1,2-epoxy-2-methylbutane (1) with PCl_5 see (1); for formn. of C̄ (together with other products) from 2-methylbutene-1 (*unsym.*-ethyl-methyl-ethylene) (1:8210) with Cl_2 at −5 to −17° see (2) (3), for formn. of C̄ (together with other products)

3:7950 3-CHLORO-3-METHYLHEXANE $C_7H_{15}Cl$ Beil. I —
(Ethyl-methyl-*n*-propyl-carbinyl chloride) I_1-(58) I_2-(119)

$$CH_3.CH_2.CH_2—\overset{Cl}{\underset{CH_3}{C}}—CH_2.CH_3$$

B.P. abt. 135° (1)	D_4^{20} = 0.8787 (4)	n_D^{20} = 1.4250 (2)
62–63° at 52 mm. (2)		1.4283 (3)
41° at 20 mm. (3)		n_D^{18} = 1.4280 (5)
39–40° at 15 mm. (4)		1.4275 (5)
32.0–32.5° at 12 mm. (5)	D_4^{14} = 0.875 (5)	n_D^{15} = 1.42705 (4)
	0.872 (5)	

[For prepn. of C̄ from 3-methylhexanol-3 (ethyl-methyl-*n*-propyl-carbinol) {Beil. I-416, I_1-(206), I_2-(445)} (2) with dry HCl at 10–15° (90% yield (2)) or with HCl (4) see (2) (4); for formn. of C̄ as a by-product of the reactn. of the above carbinol with C_6H_6 + $AlCl_3$ (main prod. 45% yield of 3-methyl-3-phenylhexane, b.p. 106–107° at 20 mm., n_D^{20} = 1.4964) see (3); for formn. of C̄ from 3-methylhexene-2 (1:8322) with conc. HCl see (5); for formn. of C̄ from ethyl-methyl-*n*-propyl-carbinyl isocyanate on htg with conc. HCl see (1).]

[For data on density and parachor of C̄ at 0°, 15°, 25°, 50°, and 65° see (6).]

C̄ with Mg in dry ether as specified (2) gives 67–78% yield corresponding RMgCl.

[C̄ converted as above to RMgCl, treated with formaldehyde gas, gives (30% yield (2)) 2-ethyl-2-methylpentanol-1, b.p. 75.5–76.0° at 15 mm., n_D^{20} = 1.4353 (2).]

C̄ with C_6H_6 + $AlCl_3$ yields (4) 3-methyl-3-phenylhexane, b.p. 110–112° at 15 mm., D_4^{20} = 0.8819, n_D^{15} = 1.49951 (4).

3:7950 (1) Montagne, *Ann. chim.* (10) **13**, 125 (1930). (2) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1561, 1565 (1933). (3) Huston, Fox, Binder, *J. Org. Chem.* **3**, 253 (1939). (4) Halse, *J. prakt. Chem.* (2) **89**, 452–453 (1914). (5) Nasarov, *Ber.* **70**, 622 (1937). (6) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3108 (1939).

3:7955 1-CHLOROHEXANE $CH_3.(CH_2)_4.CH_2Cl$ $C_6H_{13}Cl$ Beil. I - 143
(*n*-Hexyl chloride) I_1-(51) I_2-(109)

B.P.			
135–136° (1)	D_4^{20} = 0.8784 (18)	n_D^{20} = 1.42364 (1)
134–135° cor. at 763 mm. (2) (3)	0.8765 (7)	1.4200 (4)
134° at 759 mm. (18)	0.87551 (8)	1.41991 (18)
134° at 738 mm. (4)		1.41944 (6)
133.6–134.4° (5)		
132.9° at 764.7 mm. (6)		
132.7–133.3° (15)		
132–133° at 760 mm. (7)		

Colorless mobile liq., insol. aq.

[For prepn. of C̄ from hexanol-1 (1:6230) by htg. with fumg. HCl in s.t. at 100° (100% yield) see (2); by shaking with HCl + $ZnCl_2$ for 2 days (45% yield), with PCl_3 + $ZnCl_2$ (61% yield), with PCl_5 + $ZnCl_2$ (77% yield), or with excess $SOCl_2$ (yield: 85–87% (1), 63% (18) see (1) (18)); for prepn. from 1-chlorohexene-2 by cat. reductn. see (9).]

[For formation (besides other products) from *n*-hexane by chlorination see (10) (11) (12) (13); for formation from heavy metal *n*-caproates + Cl_2 see (14).]

3:7935 (1) Justoni, *Chimica e industria (Italy)* **24**, 89–94 (1942); *Cent.* **1943**, I 383. (2) Hanriot, Reynaud, *Bull. soc. chim.* (3) **21**, 14–15 (1899). (3) Demetre-Vladesco, *Bull. soc. chim.* (3) **6**, 834–835 (1891). (4) Justoni, *Chimica e industria (Italy)* **24**, 195–201 (1942); *Cent.* **1943**, I 1659.

3:7945 2-CHLORO-2-METHYLHEXANE (*n*-Butyl-dimethyl-carbinyl chloride) $C_7H_{15}Cl$ Beil. I - 156, I_1—, I_2—

$$CH_3CH_2.CH_2.CH_2{-}\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}{-}CH_3$$

B.P.			D / n	
135° sl. dec.	(1)		$D_4^{25} = 0.8661$ (6)	
130–135° sl. dec.	(2)			
133° dec. at 734 mm.	(3)		$D_4^{20} = 0.8698$ (6)	$n_D^{20} = 1.4205$ (6) (3)
132° at 740 mm.	(4)		0.863 (3)	1.4202 (5)
69–72° at 90 mm.	(5)			
58–59° at 50 mm.	(8)			
39–40° at 20 mm.	(4)			
35–35.5° at 15.5 mm.	(6)			

[For prepn. of $\bar{C}$ from 2-methylhexanol-2 (*n*-butyl-dimethyl-carbinol) [Beil. I-415, I_1-(444)] (5) (6) with dry HCl gas at −10° (65–75% yield (6)) or at 10–15° (75% yield (5)) (8), with conc. HCl (1), or with AcCl (1) (2) see indic. refs.; for formn. of $\bar{C}$ as by-product during reactn. of the above carbinol with C_6H_6 + $AlCl_3$ (main prod. 45% yield of 2-methyl-2-phenylhexane, b.p. 106–109° at 20 mm.) see (4); for prepn. of $\bar{C}$ from 2-methylhexanol-3 (isopropyl-*n*-propyl-carbinol) [Beil. I-416, I_1-(206)] (3) with dry HCl at 0° (80% yield (3)) by rearrangement see (3).]

[For data on density and parachor of $\bar{C}$ at 25°, 50°, and 75° see (7).]

$\bar{C}$ with Mg in dry ether as specified (5) gives 74.4% yield corresponding RMgCl.

$\bar{C}$ converted (as above) to RMgCl and the latter oxidized with O_2 gives (42% yield (3)) 2-methylhexanol-2, b.p. 139.5–140.5° at 741 mm., 110° at 250 mm., $D_4^{20} = 0.813$, $n_D^{20} = 1.4173$ (3).

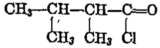
[For reactn. of RMgCl with ethyl chloroformate (3:7295) yielding (5) ethyl *n*-butyl-dimethyl-acetate, b.p. 66.5–70.0° at 16 mm., $n_D^{20} = 1.4148$ (5) (corresp. amide, m.p. 92.8–93.8° (5)) see (5); for reactn. of RMgCl with AcCl (3:7065) giving (9% yield (5)) 3,3-dimethylheptanone-2, b.p. 68–70.5° at 20 mm., $n_D^{20} = 1.4206$ (semicarbazone, m.p. 129–130°) (5) see (5).]

$\bar{C}$ converted to RMgCl and treated with CO_2 gives (5) *n*-butyl-dimethylacetic acid (constants not given (5)) (corresp. amide via acid chloride, m.p. 92.8–93.8° u.c. (5)).

3:7945 (1) Henry, de Wael, *Bull. acad. roy. Belg.* **1908**, 957–963; *Cent.* **1909**, I 1854; *Rec. trav. chim.* **28**, 448 (1909). (2) Muset, *Bull. acad. roy. Belg.* **1906**, 775–789; *Cent.* **1907**, I 1313. (3) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2266 (1938). (4) Huston, Fox, Binder, *J. Org. Chem.* **3**, 252 (1939). (5) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1559–1567 (1933). (6) Whitmore, Woodburn, *J. Am. Chem. Soc.* **55**, 363–364 (1933). (7) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3108 (1939). (8) Petrov, Kurbskii, *J. Gen. Chem. (U.S.S.R.)* **14**, 492–494 (1944); *C.A.* **39**, 4600 (1945).

(1938). (9) Mooradian, Cloke, *J. Am. Chem. Soc.* **68**, 787 (1946). (10) Kleinfeller, *Ber.* **62**, 1595–1596 (1929).
(11) Cloke, Stehr, Steadman, Westcott, *J. Am. Chem. Soc.* **67**, 1588 (1945).

3:7965 ***d,l*-α,β-DIMETHYL-*n*-BUTYRYL CHLORIDE** $C_6H_{11}OCl$ Beil. S.N. 162
(Isopropyl-methyl-acetyl chloride)

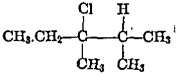


B.P. 135.9–136.6° at 751 mm. (1) D_4^{20} = 0.9795 (1)
38–39° at 18 mm. (2) D_4^{0} = 0.9961 (1)

[For prepn. of $\bar{C}$ from 2,3-dimethylbutanoic acid-1 (1:1114) with $SOCl_2$ see (1).]
$\bar{C}$ on hydrolysis yields 2,3-dimethylbutanoic acid (1:1114) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\bar{C}$ see 1:1114).

3:7965 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Nenitzescu, Chicos, *Ber.* **68**, 1587 (1935).

3:7970 3-CHLORO-2,3-DIMETHYLPENTANE $C_7H_{15}Cl$ Beil. I-157
(Ethyl-isopropyl-methyl-carbinyl chloride) I_1— I_2—

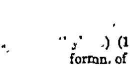


B.P. 135–138° at 757 mm. (1) D_{22}^{22} = 0.884 (1)
133–138° sl. dec. (2)
41–42° at 20 mm. (3) D_0^{0} = 0.899 (1)

[For prepn. of $\bar{C}$ from 2,3-dimethylpentanol-3 (ethyl-isopropyl-methyl-carbinol [Beil. I-417, I_1-(207), I_2-(446)] with HCl (1) or dry HCl at 0° (50% yield (2)) see (1) (2); for formn. of $\bar{C}$ from reactn. of the above carbinol with C_6H_6 + $AlCl_3$ (14% yield accompanied by 22% yield 2,3-dimethyl-2-phenylpentane) see (3).]

3:7970 (1) Kaschirsky, *J. Russ. Phys.-Chem. Soc.* **13**, 90 (1881); *Ber.* **11**, 985 (1878). (2) Whitmore, Evers, *J. Am. Chem. Soc.* **55**, 813–814 (1933). (3) Huston, Fox, Binder, *J. Org. Chem.* **3**, 253 (1939).

3:7975 *d,l*-2,3-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I-135
(Trimethylethylene dichloride; *ter*-amylene dichloride) I_1-(47) I_2-(101)



B.P. 137°		(1)		n_D^{18} = 1.445 (1)
134–138°	at	735 mm. (2)	D_4^{15} = 1.068 (1);	n_α^{15} = 1.4421 (3)
60°	at	60 mm. (11)	1.0696 (3)	n_β^{15} = 1.4566 (3)
37.0–37.5°	at	20 mm. (3)		
35–37°	at	18–20 mm. (4)		
33–35°	at	17 mm. (5)		

[For prepn. of $\bar{C}$ from 2-methylbuten[illegible]) (1 [illegible] low temp. (6) (7) (8) (3) or SO_2Cl_2 at 0° (9) [illegible] formn. of $\bar{C}$ [illegible]

$\bar{C}$ on refluxing with 10% aq. NaOH yields (9) *n*-hexanol (1:6230).

[For study of reaction of $\bar{C}$ with KI in acetone see (15); with metallic Na see (16); with NaC_2H_5 see (4); with CH_3NH_2 see (17).]

$\bar{C}$ with Mg in dry ether + trace I_2 gives (97.2% yield (19)) RMgCl.

—— *N*-(*n*-Hexyl)tetrachlorophthalimide: lfts. from EtOH, m.p. 150–151° (20). [From $\bar{C}$ (?) or from *n*-hexyl bromide with K tetrachlorophthalimide (20).]

3:7955 (1) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III, 77–89 (1929). (2) Henry, *Bull. acad. roy. Bel*
(4) Whitmore
268 (1933).
(7) Olivier, *I*
McNamee, *J. Am. Chem. Soc.* **54**, 1648–1651 (1932). (10) Schorlemmer, *Ann.* **161**, 272 (1872). (11) Michael, Turner, *Ber.* **39**, 2154–2156 (1906). (12) Ger. 261,677; June 27, 1913; *Cent.* **1913**, II 325. (13) Wertyporoch, *Ber.* **66**, 732–739 (1933). (14) C. Hunsdiecker, H. Hunsdiecker, Vogt, U.S. 2,176,181, October 17, 1939, *C.A.* **34**, 1686 (1940); Brit. 456,565, Dec. 10, 1936, French 803,941, Oct. 12, 1936, *Cent.* **1937**, I 2258. (15) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (16) Morton, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 1697–1701 (1936). (17) Westphal, Jerchel, *Ber.* **73**, 1007 (1940). (18) Vogel, *J. Chem. Soc.* **1943**, 638,640. (19) Houben, Boedler, Fischer, *Ber.* **69**, 1766, 1777 (1936). (20) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934)

3:7960 1,3-DICHLORO-2-METHYLPROPANE

$$\begin{array}{c} CH_3 \\ | \\ ClCH_2.C.CH_2Cl \\ | \\ H \end{array}$$

$C_4H_8Cl_2$ Beil. I — I_1— I_2-(88)

B.P.

136.0°	at 760 mm. (1) (2) (3)	$D_{20}^{20} = $ **1.131** (3)	$n_D^{19} = $ **1.4627** (4)
135.5°–136.5°	(9)		
131.5–132.5°	at 721 mm. (4)		
24.5°	at 10 mm. (1)		

[For prepn. by chlorination of isobutane see (3) (5) (6); from 3-chloro-2-(chloromethyl)-propene-1 (3.5633) or from 1,3-dichloro-2-(chloromethyl)propene-1 (3.9066) with H_2 + Pt black in alc. soln. see (10).]

$\bar{C}$ on htg. in s.t. at 180° with anhyd. NaOAc + AcOH yields corresp. diacetate, and this on alcoholysis by htg. with 3% dry HCl in dry MeOH gave an overall yield of 60% of the glycol, 2-methylpropanediol-1,3 [Beil. I-480], b.p. 213–214°, $D_4^{20} = 1.0290$, $n_D^{20} = 1.4445$ (6).

[For study of further chlorination of $\bar{C}$ see (7); note that $\bar{C}$ with Cl_2 or with SO_2Cl_2 + Bz_2O_2 gives (73% yield (9)) 1,2,3-trichloro-2-methylpropane (3.5885).]

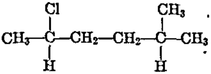
$\bar{C}$ on treatment with Zn dust in 85% alc. gives 38% yield 2-methylpropene-1, (isobutylene) (8).

[$\bar{C}$ with aq. alc. NaCN as directed (11) gives 20.4% yield γ-chloro-β-methyl-*n*-butyronitrile, b.p. 82–83° at 16 mm., $D_4^{20} = 1.042$, $n_D^{20} = 1.44255$, accompanied by 11.5% yield of β-methyl glutaro(di)nitrile, b.p. 133–137° at 16 mm. (11).]

3:7960 (1) Hass, *J. Chem. Education* **13**, 493 (1936). (2) Hass, McBee, Weber, *Ind. Eng. Chem.* **27**, 1191 (1935). (3) Ha
1935; *Cent.* **1936**, I 3012
Hass, McBee (to Purdue
(6) Hass, McBee, Weber
Soc. **58**, 1027–1029 (1936). (8) Lott, Christiansen, Schakell, *J. Am. Pharm. Assoc.* **27**, 125–130

3:7980 (1) Chattaway, Saerens, *J. Chem. Soc.* **117**, 708–711 (1920). (2) Kohlrausch, Sabathy, *Monatsh.* **72**, 307 (1939). (3) Hamilton, Sly, *J. Am. Chem. Soc.* **47**, 436–437 (1925) (4) Carré, *Bull. soc. chim.* (5) **3**, 1069 (1936). (5) Weizmann, Garrard, *J. Chem. Soc.* **117**, 328 (1920). (6) Dox, *J. Am. Chem. Soc.* **48**, 1954 (1926).

3:7985 5-CHLORO-2-METHYLHEXANE $C_7H_{15}Cl$ Beil. I - 156
(Isoamyl-methyl-carbinyl chloride) I_1— I_2—



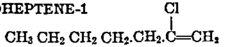
B.P. **138°** dec. at 735 mm. (1) D_4^{20} = **0.863** (1)
135–137° (2)

[For prepn. of C̄ from 2-methylhexanol-5 (isoamyl-methyl-carbinol) [Beil. I-416, I_1-(206), I_1-(445)] by saturation with dry HCl and stdg. for 6 weeks (90% yield (1)) or htg. in s.t. at 140° (2) see indic. refs.]

C̄ on conversion with Mg in dry ether to RMgCl and treatment with O_2 gives (60% yield (1)) 2-methylhexanol-5, b.p. 151–152° at 736 mm., n_D^{20} = 1.4180 (*N*-(α-naphthyl)-carbamate), m.p. 84–85° (1).

3:7985 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2267 (1938). (2) Rohn, *Ann.* **190**, 312–313 (1877).

3:7988 2-CHLOROHEPTENE-1 $C_7H_{13}Cl$ Beil. S.N. 11



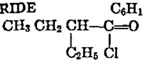
B.P. **138–139°** at 748 mm. (1) D_4^{24} = **0.8788** (1) n_D^{24} = **1.4302** (1)
71–72° at 75 mm. (1) (2)
D_4^{20} = **0.8895** (2) n_D^{20} = **1.4349** (2)

[For prepn. of C̄ from *n*-amyl methyl ketone (heptanone-2) (1:5460) with PCl_5 in C_6H_6 (40% yield together with 23% yield 2,2-dichloroheptane (3:9424)) see (2); for prepn. from heptyne-1 (1:8085) + AcCl + $SnCl_4$ see (2) (both *cis*-4-chlorononen-3-one-2, b.p. 99° at 10 mm., D_4^{25} = 0.9830, n_D^{25} = 1.4607, and *trans*-4-chlorononen-3-one-2, b.p. 89° at 10 mm., D_4^{25} = 0.9752, n_D^{25} = 1.4665 are also formed (1)).]

C̄ with powdered KOH in mineral oil at 250° does *not* (2) yield heptyne-1 (dif. from 1-chloroheptene-1 (3:8219)).

3:7988 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163–169 (1936). (2) Bachmann, Hill, *J. Am. Chem. Soc.* **56**, 2730–2732 (1934).

3:7990 α-ETHYL-*n*-BUTYRYL CHLORIDE $C_6H_{11}OCl$ Beil. II - 334
(Diethylacetyl chloride) II_1— II_2-(292)



B.P. **138.0–138.8°** at 750 mm. (1) D_4^{20} = **0.9825** (1) n_D^{20} = **1.4234** (3);
134–137° (2) **1.4239** (3)
71° at 88 mm. (3) D_4^{0} = **0.9992** (1)
40° at 20 mm. (3)

[For prepn. of C̄ from 2-ethylbutanoic acid (1:1115) with PCl_5 (2), or with $SOCl_2$ (1) (85–90% yield (3)) see indic. refs.]

(isopentane) (1:8500) (4) (10) or from 2-chloro-2-methylbutane (*ter*-amyl chloride) (3:7220) (11) with Cl_2 see indic. refs.; for formn. of C̃ from 2-methylbutene-1 (*unsym.*-ethyl-methyl-ethylene (1:8210) + Cl_2 see (12); for formn. of C̃ from 3-chloro-2-methylbutene-1 (3:7300) + HCl see (3); for formn. of C̃ from 2-methylbutanol-2 (*ter*-amyl alcohol) (1:6160) + Cl_2 see (1).]

[C̃ on further chlorination yields (3) 2,3,3-trichloro-2-methylbutane (3:4755) together with other prods.]

C̃ on htg. with solid KOH (3) or with alc. KOH (3) (4) loses HCl yielding 3-chloro-2-methylbutene-2 (3:7335) and other prods. — [C̃ on passing over soda-lime or burnt lime at 600° (13) or $BaCl_2$ at 300–500° at 20–50 mm. (14) yields 2-methylbutadiene-1,3 (isoprene) (1:8020).]

C̃ on boilg. with aq. or with aq. Na_2HPO_4 for 30 hrs. gave (2) only 10% hydrolysis; C̃ on boilg. with 1 mole NaOH in aq. soln. for 24 hrs. gave (2) only 17% hydrolysis, accompanied by isopropyl methyl ketone (1:5410).

C̃ on boilg. with 35 pts. aq. for 40 hrs. gave (5) complete decomposition with formn. of isopropyl methyl ketone (2-methylbutanone-3) (1:5410) q.v., b.p. 94°.

3:7975 (1) Brochet, *Ann. chim.* (7) **10**, 385 (1897). (2) Evers, Rothrock, Woodburn, Stahly, Whitmore, *J. Am. Chem. Soc.* **55**, 1137 (1933). (3) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, [illegible] (7) Ostromuislenskii, *J. Russ. P.* [illegible] (8) Badische Anilin- und Soda-Fabrik, Ger. 258,555, [illegible] ische Anilin- und Soda-Fabrik, Ger. 251,100, June 7, [illegible] *Eng. Chem.* **21**, 902 (1929). [illegible] Oct. 28, 1911; *Cent.* **1913**, *I* 1246. (12) [illegible] 067 (1938); *Cent.* **1939**, II 4221; *C.A.* **33**, [illegible] *Cent.* **1912**, I 535. (14) Badische Anilin- [illegible] *1913, I 476.*

3:7980 *n*-BUTYL CHLOROFORMATE (*n*-Butyl chlorocarbonate)

$C_5H_9O_2Cl$ Beil. III —

n-$C_4H_9.O\ CO\ Cl$ III_1—

III_2-(11)

B.P. 137.8° at 734.5 mm.	(1)	$D_4^{25} = 1.074$ (1)	$n_D^{18} = 1.4132$ (2)
137.6° at 730 mm.	(2)		
142°	*(3)*		$n_D^{8.4} = 1.417$ *(1)*
37–38° at 13 mm.	(2)		

Colorless mobile lachrymatory liq. with sharp but pleasant odor. — Insol. aq. and only slowly hydrolyzed by it even on htg. (1).

[For prepn. (35% yield (3)) from *n*-butyl alc. (1:6180) + phosgene (3:5000) see (1) (3); from di-*n*-butyl carbonate (1:3626) + PCl_5 see (2).]

C̃ on htg. with quinoline dec. at 81° (4) into *n*-butyl chloride (3:7160) + CO_2.

Ⓓ *n*-Butyl carbamate: from C̃ by shaking with conc. aq. NH_4OH (1); pr. from alc., m.p. 54° (1).

Ⓓ *n*-Butyl-*N*-phenylcarbamate (*n*-butyl carbanilate): from C̃ in ether by treatment with ether soln. of aniline (1 mole) + pyridine (1 mole) (1); pr., m.p. 65.5° (1), 61° (5). [For corresp. products from many other substituted anilines see (1).]

Ⓓ *n*-Butyl phenylcarbazate: from C̃ (3.9 g.) + phenylhydrazine (3.1 g.) + pyridine (3.1 g.) in aq. (15 ml.); after solidification of the sepg. yel. oil it is washed with aq. and recryst. from C_6H_6: white scaly cryst., m.p. 70° (6).

3,5,6-trichloro-2-methylbenzoquinone-1,4 [Beil. VII-651, VII_1-(354)], m.p. 238° (2)); from 2,4-dichloro-3-methylphenol (3:1205), from 2,6-dichloro-3-methylphenol (3:0150), and from 4,6-dichloro-3-methylphenol (3:1745) in $CHCl_3$ with Cl_2 see (1).]

[C̄ with PCl_5 yields (2) both *tris*-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 230° (2), and *bis*-(2,4,6-trichloro-3-methylphenyl) phosphate, m.p. 94.5° (2); for study of Hg, Sb, and Bi derivs. of C̄ see (2).]

[C̄ on sulfonation with fumg. H_2SO_4 (50% SO_3) at 50° yields (4) a monosulfonic acid; for condens. of C̄ with benzaldehyde-*p*-sulfonic acid and use of prod. as mothproofing agent see (5); for study of use of Na or K salts of C̄ as wood impregnants (preservatives) see (6).]

C̄ with aqua regia at 100° for 1½ hrs. gives (25% yield (3)) 3,5,6-trichloro-2-methylbenzoquinone-1,4 (see above), m.p. 233° (3).

[C̄ in aq. alk. with Me_2SO_4 yields (2) corresp. methyl ether, ndls. from alc., m.p. 46°, b.p. 258° (2); C̄ in aq. alk. with Et_2SO_4 yields (2) corresp. ethyl ether, ndls. from alc., m.p. 35.5°, b.p. 266° (2).]

—— **2,4,6-Trichloro-3-methylphenyl acetate:** m.p. 35°, b.p. 270° (2).

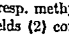
Ⓓ **2,4,6-Trichloro-3-methylphenyl benzoate:** fine prismatic pl. from alc., m.p. 53° (1). [From C̄ with BzCl in pyridine (1).]

Ⓓ **2,4,6-Trichloro-3-methylphenyl benzenesulfonate:** prismatic pl. from alc., m.p. 121° (1). [From C̄ with benzenesulfonyl chloride in pyridine (1).]

Ⓓ **2,4,6-Trichloro-3-methylphenyl *p*-toluenesulfonate:** prismatic pl. from alc., m.p. 92–93° (1). [From C̄ with *p*-toluenesulfonyl chloride in pyridine (1).]

3:0618 (1) Huston, Chen, *J. Am. Chem. Soc.* **55**, 4218 (1933). (2) Bureš, *Chem. Listy* **21**, 108–114, 148–162, 221–227, 261–265 (1927); *Cent.* **1927**, II 1345; *C.A.* **22**, 63 (1928). (3) Chulkov, Parini, Barshev, *Org. Chem. Ind (U.S.S.R.)* **3**, 410–412 (1937); *Cent.* **1938**, II 305; *C.A.* **31**, 7047 (1937). (4) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; *Cent.* **1932**, II 2371. (5) Weiler (to I.G.), Ger. 548,822, April 20, 1932; *Cent.* **1932**, II 799. (6) Iwanowski, et al., *Przemysl Chem.* **16**, 205–221 (1932); *Cent.* **1933**, I 867; *C.A.* **27**, 3796 (1933).

3:0625 2,3,6-TRICHLOROTOLUENE



$C_7H_5Cl_3$ Beil. V - 299
V_1—
V_2—

M.P. 45–46° (1)
41–42° (2)

White ndls. from alc.

[For prepn. of C̄ from 2,6-dichloro-3-aminotoluene [Beil. XII-872] via diazotization and use of Cu_2Cl_2 reactn. see (1); from *p*-toluenesulfonyl chloride via chlorination, hydrolysis to acid, and subsequent hydrolytic cleavage of the sulfonic acid radical see (3) (2); for formn. of C̄ together with other prods. from 2,5-dichlorotoluene (3:6245) or 2,6-dichlorotoluene (3:6270) with Cl_2 in pres. of Al/Hg see (4).]

[C̄ with Cl_2 in pres. of Al/Hg yields (5) 2,3,5,6-tetrachlorotoluene (3:2575).]

C̄ on mononitration by soln. in cold fumg. HNO_3 yields (1) 2,3,6-trichloro-5-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 57–58° (1); C̄ on dinitration, e.g., with 6 pts. fumg. HNO_3 + 4 pts. conc. H_2SO_4 (1), yields 2,3,6-trichloro-4,5-dinitrotoluene [Beil. V-346], pr. from AcOH, m.p. 140–142° (1), 140–141° (6).

C̄ on oxidn. with dil. HNO_3 in s.t. at 140° yields (1) 2,3,6-trichlorobenzoic acid (3:4500), m.p. 164°.

{$\bar{C}$ on htg. with sodium diethylacetate yields (2) corresp. anhydride, b.p. 230° (2).}

{$\bar{C}$ with Cl_2 yields (4) α-chloro-diethylacetyl chloride, b.p. 93° at 70 mm. (amide, m.p. 58° (4)); $\bar{C}$ with Br_2 yields (5) α-bromo-diethylacetyl *bromide*, b.p. 98–100° at 25 mm. (5); for reactn. of $\bar{C}$ with $AlCl_3 + C_6H_6$ see (6).}

{$\bar{C}$ (1 mole) upon addition to *ter*-butyl MgCl (3.7 moles) in dry ether yields (3) (by virtue of reducing actn. of the tertiary RMgX cpd.) 2-ethylbutanol-1 (1:6223), 2,2-dimethyl-4-ethylhexanol-3 (b.p. 131–132° at 150 mm., $D_{-}^{20} = 0.8339$, $n_D^{20} = 1.4340$–1.4362, *N*-(α-naphthyl)carbamate, m.p. 63–64°), and hexamethylethane (1:7090), m.p. 103° (3).}

$\bar{C}$ on hydrolysis yields 2-ethylbutanoic acid (1:1115) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\bar{C}$ see 1:1115).

3:7990 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Freund, Hermann, *Ber.* **23**, 189–190 (1890). (3) Whitmore and 11 others, *J. Am. Chem. Soc.* **63**, 646, 651–652 (1941). (4) Altwegg, Pivot, U.S. 1,493,182, May 6, 1924, *Brit.* 209,706, March 5, 1924, *Cent.* **1924**, II 1485, *C.A.* **18**, 2058 (1924). (5) Fourneau, Nicolitch, *Bull. soc. chim.* (4) **43**, 1238–1239 (1928). (6) Apolit, *Ann. chim.* (10) **2**, 80 (1924).

CHAPTER XVIII

DIVISION B. *LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE*

Section 2. D_4^{20} less than 1.1500

(3:8000–3:8499)

3:8000 3-CHLOROBUTANOL-2 (β-Butylene chlorohydrin; pseudo-butylene chlorohydrin) $CH_3—CH(Cl)—CH(OH)—CH_3$ C_4H_9OCl Beil. I - 373, I_1—, I_2-(403)

B.P. 138–140°		(1)	D_0^{18} = **1.0692** (3) (4) n_D^{20} = **1.4422** (9)
138–139°	at 753 mm.	(2)	
136.0–137.5°	at 760 mm.	(3) (4)	
134–138°		(9)	
76–79°	at 100 mm.	(5)	

[*See also d,l-erythro-3-chlorobutanol-2* (3:8004) *and d,l-threo-3-chlorobutanol-2* (3:8002).]

C̄ in this present discussion designates the ordinary mixture of stereoisomeric configurations of 3-chlorobutanol-2.

Colorless somewhat viscous liq. of agreeable odor. — C̄ is sol. at 20° in 15 vols. aq (2); its sepn. from dilute aq. solns. is best effected by steam distillation at reduced pressure (6) cf. (9).

[For prepn. of C̄ from ordinary butene-2 (mixt. of *cis* and *trans* stereoisomers) by addn. of HOCl (yields: 55% (11), 50% (3), 20% (5)) (4) (1) (2), with Cl_2 + steam at 100° (60–65% C̄ together with 10–30% 2,3-dichlorobutane (3:7615) (6)), with Cl_2 + aq. at 40–50° (50–60% yield (6)) (9), or with *N*-chlorourea in dil aq acid 15–17° in pres. of $CuCl_2$ (best yield 79.9% C̄ + 20.1% 2,3-dichlorobutane (3:7615) obtd. in 5% AcOH (7), but proportion of the two products varies widely with nature of acid used) see indic. refs.]

[For tabular and graphic data on equilibrium consts. of binary system C̄ + aq, and ternary system C̄ + 2,3-dichlorobutane (3:7615) + aq. see (8).]

C̄ in s.t. at 180°, or C̄ with aq. in s.t. at 100° for 10 hrs. or at 120° for 3 hrs., gives (80–100% yield (3)) (10) butanone-2 (ethyl methyl ketone) (1:5405) + HCl (cf. also (14)).

[C̄ with solid KOH (5), or with 40–50% aq. NaOH or KOH (15–20% excess) at 75–90° (11) (10), or with aq. KOH, K_2CO_3, or PbO at ord temp. (3) (4) (2) causes elimination of HCl and gives (yields: 87–90% (11), 75–81% (10), 66% (5)) 2,3-epoxybutane (α,β-dimethylethylene oxide) (1:6116) (mixt. of *cis* and *trans* stereoisomers)]

[The simple alkyl ethers of C̄ have been prepared by indirect means; e g., from butene-2 by action of corresp. alkyl hypochlorites dislvd. in the corresp. alc. or by action of *N,N'*-
(3-chloro-2-methoxybutane), b.p. 116°,
chloro-2-ethoxybutane), b.p. 122–124°,
ropyl, and isoamyl ethers see (12).]

—— 3-Chlorobutyl-2 acetate: b.p. 161–165° at 760 mm., 71–73° at 30 mm., D_4^{20} = 1.0692, n_D^{20} = 1.4298 (13) cf. (7). [Prepd. indirectly from ord. butene-2 with *N,N*-dichlorobenzenesulfonamide + AcOH in ether (28% yield (13)).] [For analogous prepn. of the corresp. formate, chloroacetate, and trichloroacetate see (13).]

—— 3-Chlorobutyl-2 benzoate: b.p. 263–265.5 u.c. (7).

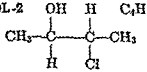
—— 3-Chlorobutyl-2 *p*-nitrobenzoate: unreported.

—— 3-Chlorobutyl-2 3,5-dinitrobenzoate: unreported.

3:8000 (1) Fourneau, Puyal, *Bull. soc. chim.* (4) **31**, 427–428 (1922). (2) Henry, *Compt. rend.* **145**, 499 (1907). (3) Krassuski, *J. Russ. Phys.-Chem. Soc.* **34**, 287–315 (1902); *Cent.* **1902**, II 20. (4) Krassuski, *Compt. rend.* **145**, 763 (1907). (5) Norton, Hass, *J. Am. Chem. Soc.* **58**, 2147 (1936). (6) Batalin, Ugryumov, *J. Gen. Chem.* (*U.S.S.R.*) **4**, 871–874 (1934); *Cent.* **1936**, I 986; *C.A.* **29**, 2147 (1935). (7) Likhosherstov, Alekseev, *J. Gen. Chem.* (*U.S.S.R.*) **3**, 927–932 (1933); *Cent.* **1934**, II 1437; *C.A.* **28**, 3053–3054 (1934). (8) Bushmakin, Gol'dman, Kuchinskaya, *Sintet. Kauchuk* **4**, No. 1, 33–35 (1935); *Cent.* **1936**, I 1131; *C.A.* **29**, 4248 (1935). (9) Batalin, Ugryumov, Tikhomirov, *Sintet. Kauchuk* **3**, No. 6, 6–12 (1934); *Cent.* **1935**, II 1935, not in *C.A.* (10) Batalin, Ugryumov, *Sintet. Kauchuk* **5**, No. 6, 8–16 (1936); *Cent.* **1936**, II 3357; *C.A.* **30**, 6701 (1936).

(11) Wilson, Lucas, *J. Am. Chem. Soc.* **58**, 2398–2399 (1936). (12) Likhosherstov, Alekseev, *J. Gen. Chem.* (*U.S.S.R.*) **4**, 1279–1282 (1934); *Cent.* **1936**, I 4287, *C.A.* **29**, 3306 (1935). (13) Likhosherstov, Petrov, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 2000–2008 (1939), *C.A.* **34**, 4380–4381 (1940). (14) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1729–1735 (1936), *Cent.* **1937**, I 3786; *C.A.* **31**, 4265 (1937).

3:8002 *d,l-threo*-3-CHLOROBUTANOL-2 C_4H_9OCl Beil. S.N. 24



B.P. 130.8° at 748 mm. (1)		D_4^{25} = 1.0586 (1)	n_D^{25} = 1.4386 (1)
52.0° at 30 mm. (1)			
51.5–52.5° at 30 mm. (2)		D_4^{20} = 1.0626 (2)	n_D^{20} = 1.4403 (2)
51.6–52.1° at 30 mm. (1)			

[*See also ord.* 3-*chlorobutanol*-2 (3:8000) *and d,l-erythro-3-chlorobutanol*-2 (3:8004).]

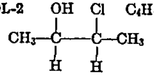
[For prepn. of $\bar{C}$ from *cis*-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (77% yield) see (1); from *cis*-butene-2 with *ter*-butyl hypochlorite (3:7165) in $AcOH/H_2SO_4$ (61% yield (1)) or with $Ca(OCl)_2$ in AcOH (2) see indic. refs.; from the diacetate of *meso*-butanediol-2,3 (1:6452) in conc. HCl contg. 1 drop conc. H_2SO_4 with large excess dry HCl gas at −10° for 90 hrs. (43% yield) see (1). — Note that $\bar{C}$ *cannot* be obtd. from butene-2 with aq. *N*-chloroacetamide (1).]

[$\bar{C}$ (1 mole) with $SOCl_2$ (1.5 moles) refluxed 3 hrs., then kept at 100° for 3 hrs. more, gives (17.4% yield (1)) *d,l*-2,3-dichlorobutane (3:7615); note, however, that $\bar{C}$ (1 mole) with $SOCl_2$ (2 moles) htd. 2 hrs. at 95° in pres. of pyridine gives (24% yield (1)) *meso*-2,3-dichlorobutane (3:7580). — Note that $\bar{C}$ with conc. HCl or with conc. HCl + $ZnCl_2$ *fails* to give any dichlorobutane; note also that $\bar{C}$ *fails* to react with 60% HBr even in s.t. at 100° for 3 hrs. (1).]

[$\bar{C}$ with very conc. aq. KOH at 90–95° loses HCl and gives (75% yield (1)) *cis*-2,3-epoxybutane (1:6116).]

3:8002 (1) Lucas, Gould, *J. Am. Chem. Soc.* **63**, 2541–2551 (1941). (2) Wilson, Lucas, *J. Am. Chem. Soc.* **58**, 2396–2402 (1936).

3:8004 *d,l-erythro*-**3-CHLOROBUTANOL-2** C_4H_9OCl **Beil. S.N. 24**



B.P. 135.4° at 748 mm. (1) D_4^{25} = 1.0610 (1) n_D^{25} = 1.4397 (1)
55.9–56.1° at 30 mm. (1)

[*See also ord.* 3-*chlorobutanol*-2 (3:8000) *and d,l-threo*-3-*chlorobutanol*-2 (3:8002).]

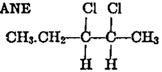
[For prepn. of C̄ from *trans*-2,3-epoxybutane (1:6116) (2 moles) with conc. HCl (3 moles) at 5° or below (82.5% yield) see (1).]

[C̄ (1 mole) with $SOCl_2$ (1.5 moles) refluxed 3 hrs., then kept at 100° for 3 more hrs. gives (16% yield (1)) *meso*-2,3-dichlorobutane (3:7580); C̄ (1 mole) in pyridine (2.2 moles) treated with $SOCl_2$ (2 moles) at 100° for 3 hrs. gives (63% yield (1)) *d,l*-2,3-dichlorobutane (3:7615), and C̄ (3 moles) with PCl_3 (1 mole) at 100° for 3 hrs. also gives (20% yield (1)) *d,l*-2,3-dichlorobutane (3:7615); note, however, that C̄ (1 mole) with PCl_5 (3.9 moles) in $CHCl_3$ refluxed 2 hrs. gives (42.7% yield (1)) a mixt. of *d,l*- and *meso*- forms of 2,3-dichlorobutane — Note that C̄ with conc. HCl or with conc. HCl + $ZnCl_2$ *fails* to give any dichlorobutane; note also that C̄ *fails* to react with 60% HBr even in s.t at 100° for 3 hrs. (1).]

[C̄ with aq. KOH loses HCl and gives (1) *trans*-2,3-epoxybutane (1:6116).]

3:8004 (1) Lucas, Gould, *J. Am. Chem. Soc.* **63**, 2541–2551 (1941).

3:8010 2,3-DICHLOROPENTANE $C_5H_{10}Cl_2$ **Beil. I - 131**
(*sym*.-Ethyl-methyl-ethylene dichloride) I_1—
I_2-(96)



B.P. 138–139.5° (1)
50–53° at 28 mm. (2)
50–51° at 20 mm. (3)

Principal component of comml. "amylene dichloride" (5).

[For prepn. of C̄ from pentene-2 (*unsym* -ethyl-methyl-ethylene) (1:8215) + Cl_2 at −17° (3) or below −5° (4) see indic. refs.; for formn. of C̄ (together with other products) from pentane (1:8505) + Cl_2 see (2) (5).]

C̄ on boilg. with 10% alc. KOH gives (2) 2-chloropentene-2 (3:7285), but C̄ with aq. K_2CO_3 gives no pentanediol-2,3 (see below).

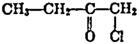
C̄ on boilg. with Zn dust in alc. or on htg. with Na in xylene at 120° gives (6) pentene-2 (1:8215).

[C̄ + aq. vapor passed at 300° over $MgCl_2$ gives (48–50% yield (7)) pentadiene-1,3 (1:8035).]

C̄ on protracted (250 hrs) boilg. with 35 pts. aq. gives (3) traces of the corresp. glycol, pentanediol-2,3 [Beil. I-482], and either or both pentanone-2 (1:5415) and/or pentanone-3 (1:5420).

3:8010 (1) Kondakov, *Ber.* **24**, 931 (1891). (2) Lemke, Tishchenko, *J. Gen. Chem. (U.S S.R.)*
(3) Froebe, Hochstetter, *Monatsh.*
J. Gen. Chem. (U.S.S.R.) **7**, 1246–
hem. **21**, 902 (1929). (6) Bourgeul,
70 (1925). (7) Lemke, Tishchenko,

3:8012 1-CHLOROBUTANONE-2 C_4H_7OCl Beil. I - 669

(Chloromethyl ethyl ketone)  I_1-(348) I_2-(731)

B.P.		B.P. (*contd.*)		
138.8–139.2° cor. at 755 mm.	(1)	67–68° at 57 mm.	(2) (9)	D_-^{13} = 1.080 (8)
137–138°	(2) (9)	65° at 50 mm.	(3)	
137.5°	(3)	63° at 40 mm.	(10)	n_-^{10} = 1.4270 (8)
135–137°	(4) (5)	59–60° at 30 mm.	(6)	
134–136°	(6)	55–56° at 30 mm.	(2)	
133–135°	(7)			
125° at 756 mm.	(8)			
124–125°	(11)			

[*See also 3-chlorobutanone-2* (3:7598).]

Liquid with penetrating odor. — Insol. aq.

[For prepn. of C̄ from ethyl methyl ketone (butanone-2) (1:5405) with Cl_2 in pres. of $CaCO_3$ + aq. (yields of C̄ about 25% always accompanied by 75% of the isomeric 3-chlorobutanone-2 (3:7598)) see (1) (3) (6) (10) (12); with Cl_2 in vapor phase (13) (14), with Cl_2 or SO_2Cl_2 in sunlight (8) (11), or with *N*-chlorourea (5) see indic. refs. — For formn. of C̄ from 1-chlorobutanol-2 (3:8025) by oxidn. with chromic acid (4), from butene-1 with HOCl (4), from 2-chloromethyl-2-ethyl-4-methyl-1,3-dioxolone-5 by hydrol. with AcOH/HCl (9), or from 2-(chloromethyl)butene-1 (3:9214) by ozonolysis (18) see indic. refs.]

[C̄ on reduction using yeast gives (15) 1-chlorobutanol-2 (3:8025).]

C̄ on oxidn. with HNO_3 (8) (11) yields chloroacetic acid (3:1370).

[C̄ on hydrolysis, e.g., by refluxing overnight with K formate in MeOH, yields (1) butanone-2-ol-1 (propionyl-carbinol) [Beil. I-826, I_1-(870)], b.p. 153–154°, 50.5–51.0° at 14 mm. (1); note, however, that C̄ with K acetate in EtOH gives (6) (8) (11) (65–70% yield (6)) propionyl-carbinyl acetate, b.p. 176° (8) (11), 178–180° (6).]

[C̄ with conc. aq KCN even in the cold yields (8) (11) the corresp. nitrile, propionylacetonitrile [Beil. III-671], b.p. 164–165° (8) (11), colorless liq., insol. aq. — C̄ with conc. aq. $(NH_4)_2SO_3$ at 70° yields (7) butanone-2-sulfonic acid-1. — C̄ with NaN_3 in aq. contg. AcOH yields (10) 1-azidobutanone-2, oil, b p. 56° at 2 mm. (10)]

[C̄ with thiourea refluxed for 2 hrs. gives (72% yield (16)) 2-amino-4-ethylthiazole hydrochloride, cryst. from alc./acetone, m.p. 185.5–187.5° u.c.; this salt with conc. aq. NH_4OH gives the free base, m.p. 35°, b.p. 118–120° at 7 mm. (16) (corresp. acetyl deriv., m.p. 117.5° u c. (16)). — C̄ with thiobenzamide + NaOAc htd in alc. gives (67% yield (17)) 4-ethyl-2-phenylthiazole, yel. cryst. from xylene, m p. 117–118° (17)]

C̄ with phenylhydrazine yields (4) a prod., yel. cryst. from AcOH, m.p. 210–215° dec., whose structure is in doubt.

Ⓓ **Chloromethyl ethyl ketone semicarbazone:** m.p. 121° (5), 120–121° (18).

Ⓓ **Condens. prod. of C̄ with *N*-methyl-β-carbohydrazidopyridinium *p*-toluenesulfonate:** cryst. from 1 1 EtOH/ether, m p. 136–137° cor. (19). [From C̄ + indicated reagent refluxed 15 min. in abs. alc. (19).]

Ⓓ **1-(Phthalimido)butanone-2:** ndls. from hot aq , m.p. 107° (12). [From C̄ with K phthalimide in dry xylene 2 hrs at b p. (27% yield (12)).]

3:8012 (1) Levene, Haller, *J. Biol. Chem.* 74, 345 (1927). (2) Blaise, *Bull. soc. chim.* (4) 15, 733 (1914). (3) Justoni, *Chimica e industria (Italy)* 24, 89-91 (1942); *Cent.* 1943, I 353. (4) de

Montmollin, Matile, *Helv. Chim. Acta* **7**, 107–109 (1924). (5) Béhal, Detoeuf, *Compt. rend.* 15?
1230 (1911). (6) Kling, *Bull. soc. chim.* (3) **33**, 325–
(7) Backer, Strating, Zuithoff, *Rec. trav. chim.* **55**,
acad. roy Belg. **1900**, 724–742; *Cent.* **1901**, I 95–96.
(10) Forster, Fierz, *J. Chem. Soc.* **93**, 675, 677 (1908).
(11) Henry, *Bull acad. roy. Belg.* **1900**, 57–63; *Cent.* **1900**, I 1123. (12) Kolshorn, *Ber.* **37**, 2474 (1904). (13) Justoni, *Chimica e industria (Italy)* **24**, 195–201 (1942); *Cent.* **1943**, I 1659. (14) I.G., French 813,131, May 26, 1937; *Cent.* **1937**, II 2071. (15) Santomauro, *Biochem. Z.* **151**, 50 (1924); *Cent.* **1924**, II 2272. (16) Bergeim, Coy, Lott, *J. Am. Chem. Soc.* **62**, 1873 (1940). (17) Friedman, Sparks, Adams, *J. Am. Chem. Soc.* **59**, 2263 (1937). (18) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1062–1067 (1938); *Cent.* **1939**, II 4221. (19) Allen, Gates, *J. Org. Chem.* **6**, 596–601 (1941).

3:8015 1,1-DICHLOROPENTANE $C_5H_{10}Cl_2$ Beil. S.N. 10

$CH_3.CH_2.CH_2.CH_2.CHCl_2$

B.P. 139.4–140.2° (1)

[For prepn. of $\bar{C}$ from isovaleraldehyde (1:0140) with PCl_5 see (1); for formn. of $\bar{C}$ (together with other prods.) from pentane (1:8505) by vapor-phase photochemical chlorination see (2).]

3:8015 (1) Kohlrausch, Köppl, *Monatsh.* **65**, 197 (1935). (2) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941).

3:8020 *d,l*-α-METHYL-*n*-VALERYL CHLORIDE $C_6H_{11}OCl$ Beil. S.N. 162

(Methyl-*n*-propyl-acetyl chloride) $CH_3.CH_2.CH_2.\underset{CH_3}{CH}.\underset{Cl}{C}{=}O$

B.P. 140.0–140.8° at 745 mm. (1) $D_4^{20} = 0.9781$ (1)
$D_4^{0} = 0.9979$ (1)

[For prepn. of $\bar{C}$ from 2-methylpentanoic acid (1:1117) with $SOCl_2$ see (1).] [The dextrorotatory isomer of $\bar{C}$ has also been reported (2).]

$\bar{C}$ on hydrolysis yields 2-methylpentanoic acid (1:1117) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\bar{C}$ see 1:1117).

3:8020 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Levene, Mikeska, *J. Biol. Chem.* **84**, 576 (1929).

3:8023 4-CHLOROHEPTENE-3 $C_7H_{13}Cl$ Beil. I - 220
I_1—
I_2-(197)

$CH_3.CH_2.CH_2.\overset{Cl}{C}{=}CH.CH_2.CH_3$

B.P. 141° (1) $D_-^{14} = 0.883$ (2) $n_D^{14} = 1.437$ (2)
138.5–139.5° cor. (2)

Two geom. stereoisomers of $\bar{C}$ are possible, but only $\bar{C}$ has yet been recognized.

[For prepn. of $\bar{C}$ from heptanone-4 (di-*n*-propyl ketone) (butyrone) (1:5447) with PCl_5 see (1) (2).]

$\bar{C}$ on treatment with $NaNH_2$ in pseudocumene at 140° yields (3) heptyne-3 (1:8095) together with a solid prod. which with aq. yields (3) heptyne-1 (1:8085).

3 [illegible]

3:8025 ***d,l*-1-CHLOROBUTANOL-2** C_4H_9OCl **Beil. I —**
(α-Butylene chlorohydrin) **I_1—**
I_2-(402)

$$CH_3.CH_2.\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}.CH_2Cl$$

B.P. 141° (1)	D_4^{25} = **1.068** (2)	n_D^{25} = **1.4410** (2)
68–70° at 27 mm. (2)		
53–55° at 17 mm. (5)	D_4^{18} = **1.040** (3)	n_D^{18} = **1.4353** (3)
52° at 15 mm. (3)		

[*See also 2-chlorobutanol-1* (3:9160).]

Colorless liq when freshly distd. but turns red on stdg. and darkens with time (3). — On distn. at ord. press. partially dec. with loss of HCl (3) [and probable formn. of 1,2-epoxybutane (see below)].

[For prepn of C̄ from butene-1 + HOCl (40–50% yield) see (1) cf. (5); from chloroacetaldehyde (3.7212) + C_2H_5MgBr in ether see (3) (5); for prepn (44% yield) by hydrolysis of corresp. trichloroacetate (obtd. by chlorination of *sec.*-butyl trichloroacetate) see (2).]

C̄ on oxidn. with CrO_3 yields (1) 1-chlorobutanone-2 (3:8012).

C̄ with hot conc. KOH gives (50% yield (1)) 1,2-epoxybutane (1:6118), b.p. 61–62° (4). [For study of this reaction see (4).]

—— **Chloromethyl-ethyl-carbinyl acetate:** unreported.
—— **Chloromethyl-ethyl-carbinyl benzoate:** unreported.
—— **Chloromethyl-ethyl-carbinyl *p*-nitrobenzoate:** unreported.
—— **Chloromethyl-ethyl-carbinyl 3,5-dinitrobenzoate:** unreported.
—— **1-(*N*-Phthalimido)butanol-2:** unreported.
Ⓓ **Chloromethyl-ethyl-carbinyl *N*-phenylcarbamate:** m.p. 78.5–79° (3).

3:8025 (1) de Montmollin, Matile, *Helv. Chim. Acta* **7**, 106–107 (1924). (2) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3363 (1939). (3) Helferich, Speidel, *Ber.* **54**, 2636–2637 (1921). (4) Moureu, Dodé, *Bull. soc. chim.* (5) **4**, 288–289 (1937). (5) Olson, Whitacre, *J. Am. Chem. Soc.* **65**, 1020 (1943).

3:8028 METHYL β-CHLOROISOCROTONATE $C_5H_7O_2Cl$ **Beil. II - 417**
II_1-(190)
II_2-(396)

$$\begin{array}{c} CH_3-C-Cl \\ \| \\ CH_3OOC-C-H \end{array}$$

B.P. 142.4° cor. (1)	D_4^{20} = **1.138** (1) (3)	
141–142° (2)	$D_4^{18.9}$ = **1.1361** (3)	$n_D^{18.9}$ = **1.45733** (3)
42–43° at 13 mm. (3)	D_-^{15} = **1.143** (1)	

[*See also methyl β-chlorocrotonate* (3:9244).]

[For prepn. of C̄ from β-chloroisocrotonic acid (3:1300) in MeOH soln. satd. with HCl gas (1) (3) or htd. with 10% conc. H_2SO_4 (yields: 70% (2), 60–62% (4)) see indic. refs.; from β-chloroisocrotonoyl chloride (see under β-chloroisocrotonic acid (3:1300)) with MeOH (yields: 90–95% (4), 80% (2)) see indic. refs.]

[C̄ with NaSH in MeOH gives (40–45% yield (2)) methyl β-mercaptocrotonate; note that the prod. is apparently a mixture of the two geometrically stereoisomeric thioenols together with the keto form, viz., methyl thioacetoacetate, $CH_3.CS.CH_2.COOCH_3$; for details see (2).]

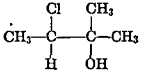
[C̄ with Na salt of ethyl mercaptan below 5° gives (80% yield (4)) a mixt. (b.p. 116–132°

at 14 mm.) of methyl β-ethylmercaptocrotonate and methyl β-ethylmercaptoisocrotonate. — $\bar{C}$ with Na salt of benzyl mercaptan gives (85% yield (4)) methyl β-benzylmercaptocrotonate, cryst. from ether or MeOH, m.p. 69–70° (4), 73° (2); note the change to the other series of stereoisomers and also that this same prod. is obtd. (78% yield (2)) from the Na thioenolate of methyl β-mercaptocrotonate with benzyl chloride.

$\bar{C}$ with hydrazine hydrate splits out HCl and MeOH with consequent ring closure yielding (5) (6) 5-methylpyrazolone-3 [Beil. XXIV-19, $XXIV_1$-(189)], m.p. 215° (5) (6).

3:8028 (1) Geuther, Frolich, *Zeit. für Chemie* **1869**, 274. (2) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) **124**, 16–20 (1930). (3) von Auwers, *Ber.* **45**, 2807 (1912). (4) Scheibler, Voss, *Ber.* **53**, 381–387 (1920). (5) Freri, *Atti V congr. nazl. chim. pura applicata, Rome* **1935**, Pt. I, 361–365 (1936); *Cent.* **1937**, I 4630; *C.A.* **31**, 3914 (1937). (6) Freri, *Gazz. chim. ital.* **66**, 25 (1936); *Cent.* **1936**, *II* 621; *C.A.* **30**, 6387 (1936).

3:8030 *d,l*-3-CHLORO-2-METHYLBUTANOL-2 $C_5H_{11}OCl$ **Beil. I - 390**
(Trimethylethylene chlorohydrin; I_1—
3-chloro-*ter*-amyl alcohol; I_2-(424)
α-chloroethyl-dimethyl-carbinol)



B.P. 141–142°	(1)	D_{22}^{22} = **1.0355**	(2)
141°	(2) (3) (4)		
139–141°	(5)	D_0^0 = **1.0562**	(2)
43–45° at 15 mm.	(5)	**1.0546**	(1)

Liq. sol. in 15–16 pts. aq. at room temp. (1).

[For prepn of $\bar{C}$ from 2-methylbutene-2 (trimethylethylene) (1:8220) with HOCl (50% yield (1) (2)) or with *N*-chlorourea in acid solution (70% yield (5)) see indic. refs.; for prepn. of $\bar{C}$ from 3-chloropentanone-2 (α-chloroethyl methyl ketone) (3:7893) (3) (4) or from ethyl α-chloropropionate (3:8125) (6) with MeMgBr (3) or MeMgI (4) see indic. refs.; note that a mixture of $\bar{C}$ with 2-chloro-2-methylbutanol-3 (3:9290) results from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-13], b.p. 75°, by ring cleavage with HCl (4).]

$\bar{C}$ on distillation over P_2O_5 (1) or on htg. at 130° with anhydrous oxalic acid (1:0535) (5) or with H_2SO_4 (92% yield (7)) gives 3-chloro-2-methylbutene-2 (trimethylvinyl chloride) (3:7335), b.p. 97–98°, + 1-chloro-2-methylbutene-2 (*β,γ-dimethylallyl chloride*) (*3:7485*), b.p. 110°.

$\bar{C}$ on boilg. with aq. + $BaCO_3$ yields (5) 2-methylbutanediol-2,3 (trimethylethylene glycol) [Beil. I-482, I_1-(251), I_2-(549)]; $\bar{C}$ on htg. with KOH (3) (6), alc. KOH (40% yield (5)), or better powdered KOH in ether (70% yield (5)) gives 2,3-epoxy-2-methylbutane (see above).

$\bar{C}$ on htg. in a s.t. with aq. at 140° (8) or by itself at 155° (8), or on htg. with aniline (70% yield (5)), gives 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410).

$\bar{C}$ with MeMgI as directed (9) yields 2,3-dimethylbutanol-2 (dimethyl-isopropyl-carbinol) (1:6187).

3:8030 ... (2) Mokiew-
... eau, Tiffeneau,
... 5 (1933). (5)
... *g.* **20**, 152–156
(1936); *Cent.* 1936, II 1178; *Rec. trav. chim.* 26, 420 (1907). (7) Groll, Burgin (to Shell Develop-
... **30**, 4875 (1936). (8) Kras-
... 19. (9) Earl, *J. Proc. Roy.*
... 9).

3:8032 1-CHLOROHEPTYNE-1 $C_7H_{11}Cl$ Beil. S.N. 12

$CH_3.CH_2.CH_2.CH_2.CH_2.C{\equiv}C{-}Cl$

B.P. 141–142° at 760 mm. (1)	$D_4^{24} = 0.9250$ (3)	$n_D^{24} = 1.4411$	(3)
65° at 49 mm. (2)			
65° at 45 mm. (3)	$D_-^{18} = 0.918$ (1) (5)	$n_D^{18} = 1.441$	(1) (5)
58.0–58.4° at 35 mm. (4)			

[For prepn. of $\bar{C}$ from heptyne-1 (*n*-amylacetylene) (1:8085) via conversion with $NaNH_2$ in ether (1) or in liq. NH_3 (4) to $C_5H_{11}.C{\equiv}C{-}Na$ and subsequent reactn. with benzenesulfonyl chloride (yield: 52% (5), 60% (1)) or *p*-toluenesulfonyl chloride (yield: 60–65% (1) (5)) see indic. refs.; via conversion with KNH_2 in liq. NH_3 (3) to $C_5H_{11}{-}C{\equiv}C.K$ and subsequent treatment with Cl_2 in dry ether at −70° see (3).]

Refractive indices of $\bar{C}$ on Pulfrich instrument: $n_C^{12.9} = 1.4402$; $n_D^{12.9} = 1.4429$; $n_F^{12.9} = 1.4492$; $n_G^{12.9} = 1.4540$ (1).

$\bar{C}$ with $HgSO_4/H_2SO_4$ gives (24–28% yield (1)) 1-chloroheptanone-2, b.p. 72–75° at 20 mm., $D_-^{20} = 0.802$, $n_D^{20} = 1.450$ (1) (see, however, different values below).

$\bar{C}$ refluxed 6 hrs. with alc. NaOEt gives (74% yield (1)) *n*-heptanoic acid (1:1140).

[$\bar{C}$ with $HgO.BF_3$ cat. in MeOH gives (30% yield (2)) 1-chloro-2,2-dimethoxyheptane, b.p. 80–82° at 8 mm., $D_4^{25} = 0.9842$, $n_D^{25} = 1.4325$ (2); this on hydrolysis with 15% HCl yields (2) 1-chloroheptanone-2, b.p. 80–82° at 13 mm., $D_4^{26} = 0.9896$, $n_D^{26} = 1.4387$ (2) (cf. values given above for prepn. by different method).]

[$\bar{C}$ with KCN in aq. MeOH gives (43% yield (2)) 1-cyano-2-methoxyheptene-1, b.p. 124–131° at 15 mm., $D_4^{25} = 0.9205$, $n_D^{25} = 1.4462$ (2) (prob. a mixt. of geom. stereoisomers).]

$\bar{C}$ fails to react with KI; after htg. 4 hrs. with 10 pts. *N* KI $\bar{C}$ was recovered unchanged (1).

3:8032 (1) Truchet, *Ann. chim.* (10) **16**, 325, 331–334, 337, 343–351 (1931). (2) Pflaum, Wenzke, *J. Am. Chem. Soc.* **56**, 1106 (1934). (3) McCusker, Vogt. *J. Am. Chem. Soc.* **59**, 1307–1309 (1937). (4) Cleveland, Murray, Taufen, *J. Chem. Phys.* **10**, 173 (1942). (5) Bourgeul, Truchet, *Compt. rend.* **190**, 754 (1930).

3:8035 *d,l*-β-METHYL-*n*-VALERYL CHLORIDE $C_6H_{11}OCl$ Beil. S.N. 162

(*sec*-Butyl-acetyl chloride)

$CH_3.CH_2.CH(CH_3).CH_2.C({=}O)Cl$

B.P. 142.5–143.0° at 749 mm. (1)	$D_4^{20} = 0.9781$	(1)
142–144° (2)		
140° at 738 mm. (3)	$D_4^{0} = 0.9963$	(1)

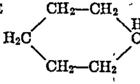
[For prepn. of $\bar{C}$ from 3-methylpentanoic acid (1:1125) with $SOCl_2$ see (1) (2) (3).]

[$\bar{C}$ with $AlCl_3 + C_6H_6$ in CS_2 gives (3) (*sec.*-butyl-acetyl)benzene (β-methyl-*n*-valerophenone, b.p. 160–161° at 50 mm. (semicarbazone, m.p. 179–180°); $\bar{C}$ with diethyl-zinc yields (2) 3-methylheptanone-5, b.p. 156.5–157.5°, $D_4^{15} = 0.825$, $n_D^{15} = 1.4159$ (semicarbazone, m.p. 101–102°).]

$\bar{C}$ on hydrolysis yields 3-methylpentanoic acid (1:1125) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\bar{C}$ see 1:1125).

3:8035 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Colonge, *Bull. soc. chim.* (4) **49**, 448 (1931). (3) Stenzl, Fichter, *Helv. Chim. Acta* **20**, 849 (1937).

3:8040 CHLOROCYCLOHEXANE (Cyclohexyl chloride)



$C_6H_{11}Cl$ Beil. V - 21
V_1-(8)
V_2-(11)

B.P.		M.P.	
143°	at 768 mm. (1)	−43.9° (4)	$D_4^{20.3}$ = 1.0000 (8)
143°	at 760 mm. (34)	−43.0° (7)	$n_D^{20.3}$ = 1.46264 (8) (13)
142.9–143.7°	at 760 mm. (2)		D_4^{12} = 1.0056 (6)
142.9°	at 760 mm. (3) (4)		n_D^{20} = 1.4626 (34)
142°	at 760 mm. (1) (5)		n_D^{12} = 1.462 (6)
141.6–142.6° cor.	at 748 mm. (6)		
141–142°	at 741 mm. (1)		
142.03°	at 740 mm. (7)		
66–68°	at 62 mm. (13)		
60.5°	at 48 mm. (3)		
42°	at 21 mm. (3)		
23–24°	at 10 mm. (23)		

Colorless liq. with somewhat penetrating but not disagreeable odor. — Volatile with steam. — Stable when pure and dry; in presence of moisture and traces of HCl, however, turns yellow, then brown (1).

[For prepn. of C̄ from cyclohexanol (1:6415) + conc. HCl under various conditions (yield: 93% (12), 90% (7), 85% (3), 60–70% (9)) see (1) (10) (7) (3) (9); from cyclohexane by chlorination with Cl_2 (11) (1) (6) (18) (33) or with SO_2Cl_2 (5) (13) see indic. refs.; from cyclohexene (1.8070) with *ter*-BuCl (3:7045) in liq. HF at 0–5° (65% yield) see (34).]

C̄ on treatment with alc. KOH (14) (6) (8), or on passing over dehydrohalogenating catalysts such as CaO, $BaCl_2$, etc., at elevated temps. (15) (16) (17) (19), or even somewhat on distillation (7), loses HCl to give cyclohexene (1:8070), b.p. 83°.

[For study of behavior of C̄ with $AlCl_3$ in CS_2 or cyclohexane see (20); for reactn. of C̄ with C_6H_6 + $AlCl_3$ to give 60–78% yield of phenylcyclohexane (1:7595), b.p. 238.7°, see (9) (21); for reactn. of C̄ with $NaOC_6H_{11}$ to yield dicyclohexyl ether, b.p. 124–126° at 10 mm., see (22); for study of reactivity of C̄ with KI (23) (24), NaOMe, pyridine, or piperidine (24) see (23) (24); for reactn. of C̄ with oxalyl chloride (3:5060) giving (60% yield (31)) hexahydrobenzoyl chloride (3:8580), b.p. 180–181° u.c., see (31).]

C̄ with Mg in dry ether gives under optimum conditions 96.5% yield (25) RMgCl; this on oxidn. with O_2 at 25° gives (81% yield (26)) cyclohexanol (1:6145) q.v., accompanied by small amts. of dicyclohexyl ether and dicyclohexyl (1:8490). [Note that C̄ on reactn. with Ag 3,5-dinitrobenzoate does *not* (27) yield expected cyclohexyl 3,5-dinitrobenzoate, m.p. 112–113°.]

- Ⓓ Cyclohexanecarboxylic acid (hexahydrobenzoic acid) (1:0575): m.p. 30–31°, b.p 233°, Neut. Eq. 128. [From RMgCl on treatment with CO_2 and subsequent acidification (85% yield (25) (28)).]
- Ⓓ Cyclohexanecarboxylic acid anilide (hexahydrobenzanilide): m.p. 146° cor. (29), 143–144° u.c. (30). [From RMgCl (30) (or RMgBr (29)) by reactn. with phenyl isocyanate.]
- Ⓓ Cyclohexanecarboxylic acid *p*-toluidide (hexahydrobenzo-*p*-toluidide): unrecorded.
- Ⓓ Cyclohexanecarboxylic acid α-naphthalide (hexahydrobenzo-α-naphthalide): m.p. 188° u.c. (32). [From R.MgBr + α-naphthyl isocyanate (32).]

3:0625 (1) Cohen, Dakin, *J. Chem. Soc.* **81**, 1331–1332 (1902). (2) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 658 (1932). (3) Geigy Co., Ger. 210,856, June 16, 1909; *Cent.* **1909**, II 79. (4) Ref. 1, pp. 1342–1343. (5) Cohen, Dakin, *J. Chem. Soc.* **85**, 1284 (1904). (6) Qvist, Holmberg, *Acta Acad. Aboensis Math. Phys.* **6**, No. 14, 3–28 (1932); *Cent.* **1932**, 2816; *C.A.* **27**, 5726–5727 (1933).

3:0655 1,2,3,4-TETRACHLOROBENZENE

$C_6H_2Cl_4$ — Beil. V - 204; V_1—; V_2-(156)

M.P. 47.5°	(4)	B.P. 254° cor. at 761.3 mm. (1)
45–46°	(1)	
45°	(2)	
44–45°	(7)	
42.0–43.3°	(3)	

Cryst. from CCl_4; spar. sol. alc; eas. sol. ether, CS_2, lgr., or 90% AcOH; sublimes.

[For prepn. of Č from 3,5-dichloro-2-nitroaniline [Beil. XII-733] via diazotization and use of Cu_2Cl_2 reactn. (note that the nitro group is *also* replaced by chloride) in 83% yield (4) see (4) (5); from 2,3,4-trichloroaniline [Beil. XII-626] via diazotization and use of Cu_2Cl_2 reaction see (7) (6) cf. (1); from 1,2,3-trichlorobenzene (3:0990) with Cl_2 in CCl_4 in pres. of Al/Hg see (7), for formn. of Č as by-prod. of actn of conc. HNO_3 on acet-2,4-dichloroanilide see (2).]

[For use of Č in mixts. of dielectric liquids see (8).]

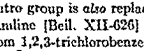
[For behavior of Č with liq. Cl_2 yielding addn. products see (9).]

[For behavior of Č with NaOMe see (4) (10).]

Č on mononitration by warming with HNO_3 ($D = 1.52$) (1) yields 1,2,3,4-tetrachloro-5-nitrobenzene [Beil. V-247], m.p. 64.5° (1), 62.0–63.5° (7), 66–67° (11); this prod. on further nitration by boilg. 2 hrs. with 10 pts. mixed HNO_3 ($D = 1.52$) + conc. H_2SO_4 yields 1,2,3,4-tetrachloro-5,6-dinitrobenzene, m.p. 151° (11).

3:0655 (1) Beilstein, Kurbatow, *Ann.* **192**, 238–239 (1878). (2) Cotts, Hunter, *J. Chem. Soc.* **125**, 447 (1924). (3) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 433 (1932). (4) Holleman, *Rec. trav. chim.* **39**, 741–743, 749 (1920). (5) Holleman, van Haeften, *Rec. trav. chim.* **40**, 70 (1921). (6) Körner, Contardi, *Atti accad. Lincei* (5) **18**, I 96 (1909). (7) Cohen, Hartley, *J. Chem. Soc.* **87**, 1365 (1905). (8) Compagnie Française Thomson-Houston, French 48,584, April 5, 1938; *Cent.* **1938**, II 906. *C.A.* **33**, 277 (1939). (9) van der Linden, *Rec. trav. chim.* **55**, 421–430 (1936). (10) de Crauw, *Rec. trav. chim.* **50**, 787 (1931).
(11) Beckmans, Holleman, *Rec. trav. chim.* **44**, 856–857 (1925).

3:0670 2,4'-DICHLOROBIPHENYL



$C_{12}H_8Cl_2$ — Beil. S.N. 479

M.P. 46° (1) B.P. 191° at 30 mm. (2)

Cryst from alc (1); sol in C_6H_6 or AcOH (1).

[For prepn. of Č from 2-amino-4'-chlorobiphenyl (2), from 4-amino-2,4'-dichlorobiphenyl (1), or 2,4'-diaminobiphenyl (1) by appropriate diazo reactions see (1) (2).]

Č on oxidn. with CrO_3 + AcOH yields (2) p-chlorobenzoic acid (3:4940), m.p. 232° (2).

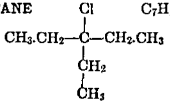
3:0670 (1) Finzi, Bellavita, *Gazz. chim. ital.* **64**, 339 (1934). (2) de Crauw, *Rec. trav. chim.* **50**, 776–777 (1931).

(1) (4) (p-nitrobenzoate, m.p. 40–41° (2); N-(p-xenyl)carbamate, m.p. 103.5° (2)) with PCl_5 (73% yield (4)) (1) (5) or with PCl_3 + pyridine at 0° (2) see indic. refs.] [The levorotatory isomer of C̄ (from dextrorotatory hepten-2-ol-4, with PCl_3 + pyridine at 0° (2)) has b.p. 44° at 14 mm., n_D^{21} = 1.4430 (2).]

[C̄ with phenol + K_2CO_3 in acetone gives (65% yield (4)) (3) phenyl α-(n-propyl)crotyl ether, b.p. 153–154° at 23 mm. (4), 103–104° at 4 mm. (3), D_{20}^{20} = 0.9282 (3), n_D^{21} = 1.5000 (3). — For studies of the rearr. of this ether on htg. see (1).] [For similar reaction of C̄ with o-cresol see (3).]

3:8050 (1) Hurd, Williams, *J. Am. Chem. Soc.* **58**, 2636–2637 (1936). (2) Arcus, Kenyon, *J. Chem. Soc.* **1938**, 1918. (3) Hurd, Puterbaugh, *J. Org. Chem.* **2**, 382–384 (1938). (4) Hurd, Cohen, *J. Am. Chem. Soc.* **53**, 1920–1922 (1931). (5) Reif, *Ber.* **41**, 2743 (1908).

3:8055 3-CHLORO-3-ETHYLPENTANE $C_7H_{15}Cl$ Beil. I — I_1-(58) I_2-(120)
(Triethylcarbinyl chloride)



B.P. 143–144°	(1)		n_D^{25} = **1.4311**	(3)
140–143°	(2)	D_{25}^{25} = **0.8951** (3)	**1.43276**	(1)
83–83.5° cor. at **100 mm.**	(3)		n_D^{20} = **1.4329**	(4)
64–65° at **52 mm.**	(4)	D_4^{25} = **0.8644** (1)	**1.4293**	(2)
43–44° at **20 mm.**	(5)		n_D^{18} = **1.4310**	(2)

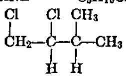
[For prepn. of C̄ from 3-ethylpentanol-3 (triethylcarbinol) (1:6218) with dry HCl at 10–15° (88% yield (4)), with HCl (1), or with conc. HCl + $ZnCl_2$ at room temp. (3) see indic. refs.; for formn. of C̄ (2% yield (5)) as by-product of reactn. of triethylcarbinol with $AlCl_3$+ C_6H_6 (main prod. is 40% yield of 3-ethyl-3-phenylpentane, b.p. 225–226° at 745 mm., 107–108° at 20 mm., n_D^{25} = 1.4953, n_D^{20} = 1.4975) see (5); for prepn. of C̄ from 3-ethylpentene-2 (1:8330) with HCl gas in AcOH (3) or with conc. or fumg. HCl (2) see (2) (3).]

C̄ with Mg in dry ether as directed (4) gives 58% yield corresp. RMgCl.

C̄ converted (as above) to RMgCl, treated with formaldehyde gas, gives (10% yield (4)) 2,2-diethylbutanol-1, b.p. 75–78° at 12 mm., n_D^{20} = 1.443 (4).

3:8055 (1) Schreiner, *J. prakt. Chem* (2) **82**, 296 (1910). (2) Nasarov, *Ber.* **70**, 623 (1937). (3) Lucas, *J. Am. Chem. Soc.* **51**, 252–253 (1929). (4) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1560–1562, 1566 (1933). (5) Huston, Fox, Binder, *J. Org. Chem.* **3**, 253 (1939).

3:8075 *d,l*-3,4-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I - 137 I_1-(47) I_2—
(Isopropylethylene dichloride)

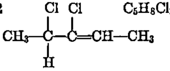


B.P. 143–145° (1) (3)
142° (2)

[For prepn. of C̄ from 3-methylbutene-1 (isopropylethylene) (1:8200) + Cl_2 see (1); for formn. (together with 1,4-dichloro-2-methylbutane (3:8360) and 2,4-dichloro-2-methylbutane (3:8105)) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) with Cl_2 in light see (2) (4).]

... , Stockmair, *Z. physik. Chem.* ... (4) Nagornov, Rotinyantz, ... I 2648, *C.A.* **21**, 3780 (1927). ... er, Mailhe, *Ann. chim.* (8) **10**, ... *Bull. soc. chim. Belg.* **48**, 255, ... Hayes, Turner, *J. Chem. Soc.* **1929**, 502. (10) I Zugravescu, S. Zugravescu, *Bul. Soc. Chim. România* **19-A**, 85–92 (1937); *Cent.* **1939**, II 1279.
...
206 (1931).
(21) Neunhoeffer, *J. prakt. Chem.* (2) **133**, 105–107 (1932). (22) Fichter, Siegrist, *Helv. Chim.* ...
Soc. **56**, 2119 (1934).
(31) Kharasch, Brown, *J Am. Chem Soc* **64**, 332 (1941). (32) Gilman, Furry, *J. Am. Chem. Soc.* **50**, 1216 (1928). (33) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945; *C.A.* **39**, 3534 (1945). (34) Simons, Meunier, *J. Am. Chem. Soc.* **65**, 1269–1271 (1943).

3:8045 *d,l*-**3,4-DICHLOROPENTENE-2** $C_5H_8Cl_2$ Beil. I-210, I_1—, I_2—



B.P. 142–144° at 736 mm. (1)

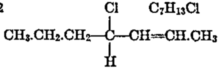
Two geom. stereoisomers of C̄ are possible, but as yet only this one is recognized.
[For prepn. of C̄ from 3-chloropenten-2-ol-4 with PCl_3 see (1).]

C̄ on boilg. with aq. is partially reconverted (1) to 3-chloropenten-2-ol-4 [Beil. I-443], b.p. 158–159° at 724.4 mm

C̄ adds Br_2 yielding (1) 2,3-dibromo-3,4-dichloropentane, b.p. 140–145° at 31 mm. (1).

3:8045 (1) Garzarolli-Thurnlackh, *Ann.* **223**, 160–161 (1884).

3:8050 *d,l*-**4-CHLOROHEPTENE-2** (Propenyl-*n*-propyl-carbinyl chloride) $C_7H_{13}Cl$ Beil. I-220, I_1—, I_2—



B.P. 140–145° (1)
140–144° (5)
86–90° at 104 mm. (5)
49° at 21 mm. (2)
46–48° at 12 mm. (3)

n_D^{21} = **1.4430** (2)
n_D^{19} = **1.4422** (3)
D_4^{18} = **0.879** (2)

Note that some evidence exists (1) that in certain reactions C̄ reacts (by virtue of allyl transposition) as its synionic isomer 2-chloroheptene-3 (but this has not itself been characterized).

[For prepn. from hepten-2-ol-4 (propenyl-*n*-propyl-carbinol) [Beil. I-447, I_1-(488)]

[C̄ with Br_2 followed by abs. alc. gives (94% yield (6)) ethyl α-bromo-isobutylacetate, b.p. 100–102° at 17 mm. (6); for study of catalytic reduction of C̄ see (7).]

C̄ on hydrolysis yields isobutylacetic acid (isocaproic acid) (1:1127) q.v. (for the amide, anilide, p-toluidide, and other derivatives corresponding to C̄ see 1:1127).

3:8090 (1) Hommelen, *Bull. soc. chim. Belg.* **42**, 243–250 (1933). (2) Kohlrausch, Pongratz, *Z. physik. Chem.* B-**22**, 383 (1933). (3) Freundler, *Bull. soc. chim.* (3) **13**, 833 (1895). (4) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (5) Curtius, Hambsch, *J. prakt. Chem.* (2) **125**, 194 (1930). (6) Guha, Muthanna, *Ber.* **71**, 2670 (1938). (7) Grignard, Mingasson, *Compt. rend.* **185**, 1173–1176 (1927). (8) Rupe, Giesler, *Helv. Chim. Acta* **11**, 664 (1928).

3:8095 ***d,l*-4-CHLOROHEPTANE** (Di-*n*-propyl-carbinyl chloride) $C_7H_{15}Cl$ Beil. I —, I_1—, I_2-(117)

$CH_3.CH_2.CH_2—CH(Cl)—CH_2.CH_2.CH_3$

B.P. 144–145° at 758 mm. (1)	D_4^{20} = **0.8710** (3)	n_D^{20} = **1.4237** (1)
143.1–144.4° at 751 mm. (2)	**0.8619** (1)	**1.4231** (3)
48.9° at 21 mm. (3)	D_4^{15} = **0.8751** (3)	**1.4199** (2)

[For prepn. of C̄ from heptanol-4 (1:6228) with conc. HCl + $ZnCl_2$ (1) (2) (3) (yield: 60–64% (3), 35% (1)) see indic. refs.]

C̄ converted to corresp. acetate by 7-hr. reflux with KOAc + AcOH, then hydrolyzed by 6-hr. boilg. with 20% alc. KOH, and the resultant heptanol-4 (1:6228) oxidized with CrO_3/H_2SO_4 gives (3) heptanone-4 (1:5447) q.v. (semicarbazone, m.p. 129° by this route, 132° from authentic heptanone-4 (3)).

C̄ with powdered or alc. KOH or NaOH slowly regenerates heptanol-4 (1:6228) without any trace of olefin (1).

3:8095 (1) Mathus, Gibon, *Bull. soc. chim. Belg.* **34**, 306 (1925). (2) Dillon, Lucas, *J. Am. Chem. Soc.* **50**, 1711–1714 (1928). (3) Sherrill, *J. Am. Chem. Soc.* **52**, 1985–1989 (1930).

3:8100 ***d,l*-2-CHLORO-2-METHYLHEPTANE** (*n*-Amyl-dimethyl-carbinyl chloride) $C_8H_{17}Cl$ Beil. I-161, I_1—, I_2—

$CH_3.CH_2.CH_2.CH_2.CH_2—C(Cl)(CH_3)—CH_3$

B.P. 140–150° dec. (1)	D_4^{25} = **0.8568** (2)	n_D^{25} = **1.4363** (4)
49.5–51° at 15 mm. (2)		
		n_D^{20} = **1.4263** (4)
		1.4257 (3)
		1.4250 (2)

C̄ decomposes very easily on distn. (cf. (3)).

[For prepn. of C̄ from 2-methylheptanol-2 (*n*-amyl-dimethyl-carbinol) [Beil. I-420, I_1-(209), I_2-(452) (2) (3)] with HCl gas (yield 81% (2), 73% (3)) or with AcCl (1) see indic. refs.]

C̄ on distn. over powdered KOH gives 2-methylheptene-2 (α,α-dimethyl-β-*n*-butyl-ethylene) [Beil. I-222, I_1-(93)], b.p. 122–123° at 755 mm., D_-^{20} = 0.816 (1).

C̄ with Mg in dry ether as directed (2) gives 59.9% yield RMgCl.

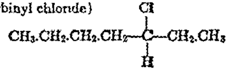
C̄ on conversion to RMgCl and subsequent treatment with CO_2 gives (in addition to much olefin) (22% yield (2)) dimethyl-*n*-amyl-acetic acid, b.p. 118°, n_D^{20} = 1.4335–1.4305 (2) (amide, m.p. 102.5–103.5° (2)).

$\bar{C}$ is scarcely attacked by K_2CO_3 (1) — $\bar{C}$ on boilg. with aq. for 100 hrs can be recovered unchanged to extent of 85%, the remainder yielding traces of 2-methylbutanediol-1,2 [Beil. I-482], 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410), and 2-methyl butyne-1 (isopropylacetylene) (1:8010) (3).

[$\bar{C}$ passed over soda-lime at 470° gives (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:8075 (1) Kondakow, *J. Russ. Phys.-Chem. Soc.* **20**, 144 (1888). (2) Perkin, *J. Soc. Chem. Ind.* **31**, 616–624 (1912). (3) *Froebe, Hochstetter, Monatsh.* **23**, *1079–1081 (1902).* (4) *Badische* Anilin- u Soda-Fabrik, Ger 261,677, March 14, 1911; *Cent* **1913**, II 325.

3:8080 *d,l*-3-CHLOROHEPTANE $C_7H_{15}Cl$ Beil. I —
(Ethyl-*n*-butyl-carbinyl chloride) I_1—
I_2-(117)



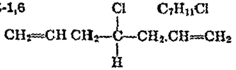
B.P. 143.4–144.4° at 751 mm. (1)	D_4^{20} = **0.8690** (2)	n_D^{20} = **1.4237** (1)
48.3° at **21** mm. (2)	D_4^{15} = **0.8732** (2)	**1.4228** (2)

[For prepn. of $\bar{C}$ from heptanol-3 [Beil. I_1-(205), I_2-(444) (2)] with conc. HCl + $ZnCl_2$ (yield 60–64% (2)), 30% (1)) see (1) (2).] [A dextrorotatory form of $\bar{C}$ has been prepd. (3) by cat. hydrogenation of levorotatory 3-chloroheptene-1: b.p 87–90° at 113 mm., n_D^{25} = 1.4221 (3).]

$\bar{C}$ converted to corresp. acetate by 7 hrs. reflux with KOAc + AcOH, then hydrolyzed by 6 hrs boilg. with 20% alc. KOH, and the resultant heptanol-3 oxidized with CrO_3/H_2SO_4 gives (2) heptanone-3 [Beil. I-699, I_1-(359), I_2-(754)] (semicarbazone, m.p. 88–89° (2)).

3:8080 (1) Dillon, Lucas, *J. Am. Chem Soc.* **50**, 1711–1714 (1928). (2) Sherrill, *J. Am. Chem. Soc.* **52**, 1985–1988 (1930). (3) Levene, Rothen, *J. Biol. Chem.* **119**, 191–192 (1937).

3:8085 4-CHLOROHEPTADIENE-1,6 $C_7H_{11}Cl$ Beil. I-257
(Diallylcarbinyl chloride) I_1—
I_2—



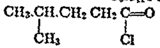
B.P. 144° dec. (1)

[For prepn of $\bar{C}$ from heptadien-1,6-ol-4 (diallylcarbinol) [Beil. I-455, I_2-(506)] with PCl_5 see (1).]

$\bar{C}$ with alc. KOH readily removes 1 HCl yielding a heptatriene, b.p. 115° (1).

3:8085 (1) Saytzeff, *Ann.* **189**, 141–145 (1877).

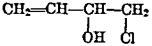
3:8090 γ-METHYL-*n*-VALERYL CHLORIDE $C_6H_{11}OCl$ Beil. II - 329
(Isocaproyl chloride, II_1—
isobutyl-acetyl chloride) II_2-(289)



B.P. 143.8–144.6° at 745 mm.	(1)	D_4^{20} = **0.9725** (1)
141.9–144.7°	(2)	
141–142°	(3)	D_4^{0} = **0.9922** (1)
[**120–130°**	(8)]	

[For prepn. of $\bar{C}$ from 4-methylpentanoic acid-1 (isocaproic acid) (1:1127) with PCl_5 (63% yield (4)), with PCl_3 + $ZnCl_2$ (68% yield (4)), or with $SOCl_2$ (1) (2) (5) (8) (82% yield (4)) see indic. refs.]

3:8110 ***d,l*-1-CHLOROBUTEN-3-OL-2** C_4H_7OCl Beil. S.N. 25
(Chloromethyl-vinyl-carbinol)



B.P.			
144–147°	**(1)**	D_4^{20} = **1.111 (3)**	n_D^{20} = **1.4660 (3)**
76° at 60 mm.	**(2)**		**1.4643 (2)**
64.0–64.8° at 30 mm.	**(3)**	D_4^{15} = **1.1214 (1)**	n_D^{15} = **1.468 (1)**

[*See also* 2-*chlorobuten*-3-ol-1 (3:9113).]

[For prepn. of C̄ from butadiene-1,3 with HOCl generated from $Ca(OCl)_2 + CO_2$ (3) or from *N*-chlorourea + acid in cold (1) (yields of C̄: 75% (1), 52% (3)) see indic. refs.]

C̄ with Br_2 in $CHCl_3$ adds 1 mole halogen giving (1) 1-chloro-3,4-dibromobutanol-2, b.p. 129–130° at 10 mm.; $D_4^{20} = 2.042$, $D_4^{15} = 2.0504$; $n_D^{20} = 1.561$, $n_D^{15} = 1.564$ (1); note that this prod. on oxidn. with $Na_2Cr_2O_7 + H_2SO_4$ at 35° gives (1) 1-chloro-3,4-dibromobutanone-2, b.p. 132–133° at 25 mm.; $D_4^{20} = 2.0521$, $D_4^{15} = 2.0589$; $n_D^{20} = 1.554$, $n_D^{15} = 1.559$ (1).

C̄ with 50% aq. NaOH at 115–185° for 1 hr. (3) or with 60% KOH (1) loses HCl ring closing to (yields: 87% (2), 84% (3)) 3,4-epoxybutene-1, b.p. 65.0–65.8° at 739 mm, $D_4^{20} = 0.875$, $n_D^{20} = 1.4170$ (3) cf. (1). [For various reactions of this product see (1) (2) (3) (4).]

[For study of rate of hydrolysis of C̄ with aq. NaOH see (2).]

—— **1-Methoxybuten-3-ol-2** (C̄ **methyl ether**): b.p. 143–144° (1) (4), 69–71° at 49 mm. (3); $D_4^{20} = 0.9470$ (1) (4); $n_D^{20} = 1.4343$ (1) (4), 1.4297 (3): corresp. 3,5-dinitrobenzoate, m.p. 70–71° (3). [From C̄ (3) or from 3,4-epoxybutene-1 (above) (1) (4) with MeOH/NaOMe in 51–52% yields (3) (1).]

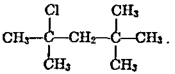
—— **1-Ethoxybuten-3-ol-2** (C̄ **ethyl ether**): b.p. 153–157°; $D_4^{15} = 0.9214$; $n_D^{15} = 1.4330$ (1) (4). [Presumably from C̄ (although not actually reported) or from 3,4-epoxybutene-1 (above) (1) (4) with EtOH/NaOEt.]

—— **1-Chlorobuten-3-yl-2 acetate**: b p. 163–166°; $D_4^{15} = 1.1308$; $n_D^{15} = 1.4610$ (1).

Ⓓ **1-Chlorobuten-3-yl-2 3,5-dinitrobenzoate**: m.p. 61.5–63 5° u.c. (3). [Note that this prod. depresses m.p. of corresp. deriv. (m.p. 65.5° u.c.) from 2-chlorobuten-3-ol-1 (3:9113).]

3:8110 (1) Petrov. *J. Gen. Chem.* (*U.S.S.R.*) **8**, 131–140 (1938); *Cent.* **1939**, I 2596; *C.A.* **32**, 5369 (1938). (2) Kadesch, *J. Am. Chem. Soc.* **68**, 46–48 (1946). (3) Kadesch, *J. Am. Chem. Soc.* **68**, 41–45 (1946). (4) Petrov, *Acta Univ. Voronegiensis* **8**, No. 2, 71–79 (1935); *Cent.* **1936**, II 2333–2334; *C.A.* **32**, 4524 (1938).

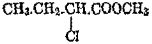
3:8113 4-CHLORO-2,2,4-TRIMETHYLPENTANE $C_8H_{17}Cl$ Beil. I-164
(Di-isobutylene hydrochloride) I_1—
I_2—



B.P.		M.P.		
145–150° dec.	**(1)**	**−26° (4)**	D_-^{18} = **0.8756 (2)**	n_D^{24} = **1.4286 (6)**
62.8° at 40 mm.	**(6)**			
44° at 16 mm.	**(5)**		D_0^0 = **0.8891 (2)**	n_D^{20} = **1.4307 (5)**
40° at 13 mm.	**(2)**			

3:8100 (1) Muset, *Bull. acad. roy. Belg.* **1906**, 775–789; *Cent.* **1907**, I 1313; *C.A.* **1**, 1696 (1907). (2) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1559–1567 (1933). (3) Whitmore, Williams, *J. Am. Chem. Soc.* **55**, 409 (1933). (4) Smart, Quayle, *J. Am. Chem. Soc.* **67**, 21–23 (1945).

3:8103 METHYL *d,l*-α-CHLORO-*n*-BUTYRATE $C_5H_9O_2Cl$ Beil. II - 277
II₁—
II₂—

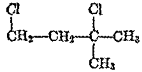


B.P. 145–146° at 756 mm. (1) D_-^{14} = 1.0979 (1) n_D^{14} = 1.42526 (1)

[For prepn. of C̄ from α-chloro-*n*-butyronitrile with MeOH + HCl see (1).] For the amide corresp. to C̄ see α-chloro-*n*-butyric acid (3:9130).

3:8103 (1) Henry, *Bull. acad. roy. Belg.* (3) **35**, 507–520 (1898); *Cent.* **1898**, I 273.

3:8105 2,4-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I - 135
(Isoprene *bis*-hydrochloride) I₁-(47)
I₂—



B.P. 145–146°	(1)	D_4^{20} = 1.0654 (1) n_D^{20} = 1.44549 (5)
144–148°	(5)	
142°	(2)	
52–53° at 12 mm.	(1)	
39° at 10 mm.	(5)	

[Earlier work on this compd. seems now to have been carried out on impure material and should be disregarded.]

[For prepn. of C̄ from 4-chloro-2-methylbutene-2 (isoprene monohydrochloride) (3:7465) with conc. HCl satd. with HCl gas see (1) (5); for prepn. of C̄ from 2-methylbutadiene-1,3 (isoprene) (1.8020) with conc. HCl see (2) (5); for formn. of C̄ from 2-methylbutane (isopentane) (1·8500) (together with 2,3-dichloro-2-methylbutane (3.7975) and 1,4-dichloro-2-methylbutane (3·8360)) see (3), for formn. of C̄ (together with 1,4-dichloro-2-methylbutane (3:8360) and 3,4-dichloro-2-methylbutane (3:8075)) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) + Cl_2 in light see (4).]

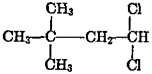
C̄ on hydrolysis with boilg. 20% K_2CO_3 (3) or 20% aq. NaOH (5) gives 2-methylbutane-diol-2,4 [Beil. I-483, I₁-(251)], b.p. 108° at 16–17 mm., D_{20}^{20} = 0.9852, n_D^{20} = 1.4434 [*N,N*-*bis* (phenylcarbamate), m.p. 113.8–114.6°] (3) cf. (5).

C̄ on oxidn. with $KMnO_4$ yields (3) β-hydroxyisovaleric acid [Beil. III-327, III₁-(122)].

3:8105 (1) Aschan, *Ber.* **51**, 1307 (1918). (2) Ostromuislenskii, *J. Russ. Phys.-Chem. Soc.* **47**, 1983–1988 (1915), *Cent* **1916**, II 307, *C.A.* **10**, 1341 (1916). (3) Davydova, Papkina, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1992–1994 (1937); *Cent.* **1939**, I 2397; *C.A.* **32**, 482 (1938). (4) Perkin, *J. Soc. Chem. Ind.* **31**, 616–624 (1912). (5) Soday (to United Gas Improvement Co.), U.S. 2,376,396, May 22, 1945; *C.A.* **39**, 3548–3549 (1945).

(21) Drushel, *Am. J. Sci.* (4) **34**, 69–74 (1912); *Cent.* **1912**, II 704; *C.A.* **6**, 2593 (1912). (22) Bolin, *Z. anorg. allgem. Chem.* **177**, 246–248 (1929).

3:8132 4,4-DICHLORO-2,2-DIMETHYLBUTANE $C_6H_{12}Cl_2$ Beil. S.N. 10
(1,1-Dichloro-3,3-dimethylbutane)



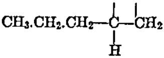
B.P.	M.P.		
148° (1)	**−56.5°/−56.0° (1)**	D_4^{20} = **1.0262 (1)**	n_4^{20} = **1.4389 (1)**

[For prepn. of $\bar{C}$ from vinyl chloride (3:7010) with 2-methylbutane (isobutane) + $AlCl_3$ at −10° (40% yield) or with *ter*-butyl chloride (3:7045) see (1).]

$\bar{C}$ with aq. in s.t. at 300° hydrolyzes to *ter*-butylacetaldehyde, b.p. 102–103° (corresp. methone, m.p. 162–163°; corresp. 2,4-dinitrophenylhydrazone, m.p. 146–147°) (1).

3:8132 (1) Schmerling, *J. Am. Chem. Soc.* **67**, 1438–1441 (1945).

3:8140 *d,l*-1,2-DICHLOROPENTANE $C_5H_{10}Cl_2$ Beil. I —
I_1—
I_2-(95)



B.P.	**148.4–148.8°**	(1)	D_{25}^{25} = **1.0773** (2)	n_D^{25} = **1.4453** (2)
	146.0–146.2°	(2)	**1.0667** (2)	**1.4448** (2)
	145.8–146.2° at 739 mm.	(2)		
	58–59° at 28 mm.	(3)	D_4^{20} = **1.0872** (1)	n_D^{20} = **1.4485** (1)

Colorless oil, insol. aq , volatile with steam.

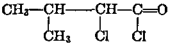
[For prepn. of $\bar{C}$ (70% yield (2)) from 1-chloropentanol-2 (3:8225) with $SOCl_2$ + diethylaniline or from pentene-1 (1:8205) in CCl_4 at 0°+Cl_2 (50% yield (2)) (1) see (1) (2).]

[For formn. of $\bar{C}$ (together with other prods.) from pentane (1:8505) (3) or from 1-chloropentane (3:7460) (4) with Cl_2 see indic. refs.]

$\bar{C}$ with alc. KOH gives (3) 1-chloropentene-1 (3:7420), but $\bar{C}$ with K_2CO_3 does *not* (3) yield the corresp. glycol.

3:8140 (1) Tishchenko, Shchigel'skaya, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1246–1248 (1937); *Cent.* **1938**, II 2576; *C.A.* **31**, 6189 (1937). (2) Koelsch, McElvain, *J. Am. Chem. Soc.* **51**, 3393–3394 (1929). (3) Lemke, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1995–1998 (1937); *Cent.* **1939**, I 2398; *C.A.* **32**, 482 (1938). (4) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941).

3:8144 *d,l*-α-CHLORO-ISOVALERYL CHLORIDE $C_5H_8OCl_2$ Beil. II-316
(α-Chloro-β-methyl-*n*-butyryl chloride) II_1—
II_2—



B.P. 148–149° (1) $D_{-}^{13.2}$ = **1.135 (1)**

[For prepn. of $\bar{C}$ from α-chloro-isovaleric acid (3:0050) with PCl_3 see (1).]

$\bar{C}$ on hydrolysis with aq. yields α-chloro-isovaleric acid (3:0050).

3:8144 (1) Servais, *Rec. trav. chim.* **20**, 53 (1901).

Colorless mobile liq. with characteristic odor.

[For prepn. from 2,4,4-trimethylpentene-1 (1:8340) or 2,4,4-trimethylpentene-2 (1:8345) ("diisobutylene") with conc HCl (satd. at −20°) in s.t. at 100° (1) (2), with HCl gas in cold (5) or at −10° to −25° in pres. of $ZnCl_2$ (4) (*almost quant. yield* (5)) *see indic. refs.*]

C̄ on distillation loses HCl and regenerates "diisobutylene" (4) (2).

C̄ with alc. KOH yields diisobutylene (see above).

[For reactn. of C̄ with phenol + alc. $NaOC_6H_5$ yielding phenyl diisobutyl ether, b.p. 250–260° see (3); note, however, that this prod. in s.t. at 250° for 2 hrs. rearr. to *p*-(di-isobutyl)phenol, m.p. 84° (3).]

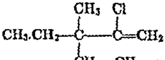
[For reaction of C̄ with $(CH_3)_2Zn$ yielding 2,2,4,4-tetramethylpentane (1:8645), b.p. 122.3°, $n_D^{25} = 1.4051$, see (4).]

[For reactn. of C̄ with silver cyanate, followed by alk. hydrolysis to yield 4-amino-2,2,4-trimethylpentane (acetyl deriv., m.p. 99°; reactn. prod. with phenyl isocyanate, m.p. 137°) *see* (5).]

[C̄ with 2-methyl butane (isopentane) (1:8500) + $AlCl_3$ shaken for 2 min. gives (6) 2-chloro-2-methylbutane (*ter*-amyl chloride) (3 7220).]

3:8113 (1) Butlerow, *Ann.* **189**, 51–53 (1877). (2) Kondakov, *J Russ. Phys.-Chem. Soc.* **28**, 790 (1896). *J prakt Chem* (2) **54**, 449–450 (1896) (3) Natelson, *J. Am. Chem. Soc.* **56**, 1585 (1934). (4) Howard, *J. Research Nat'l Bur Standards* **24**, 678–679, 681 (1940). (5) Whitmore, Wilson, Capinjola, Tongberg, Fleming, McGrew, Cosby, *J. Am. Chem. Soc.* **63**, 2041 (1941). (6) Bartlett, Condon, Schneider, *J. Am. Chem Soc* **66**, 1537 (1944).

3:8115 2-CHLORO-3-ETHYL-3-METHYLPENTENE-1 $C_8H_{15}Cl$ **Beil. S.N. 11**



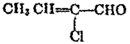
B.P. 147° at 743 mm. (1) n_D^{25} **= 1.4450 (1)**
53° at 20 mm. (1) D_4^{20} **= 0.9147 (1)**

[For prepn of C̄ from 3-ethyl-3-methylpentanone-2 [Beil. I_2-(760)] (1) with PCl_5 (65% yield) see (1).]

C̄ with $NaNH_2$ in mineral oil at 160–165° gives 45% yield 3-ethyl-3-methyl-pentyne-1, b.p. 98–100° at 745 mm., $D_4^{20} = 0.7360$, $n_D^{20} = 1.4102$ (Ag salt, darkens 167°, melts 191.5°) (1).

3:8115 (1) Davis, Marvel, *J. Am. Chem. Soc.* **53**, 3844–3845 (1931).

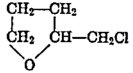
3:8117 α-CHLOROCROTONALDEHYDE C_4H_5OCl **Beil. I - 731**
(2-Chlorobuten-2-al-1) I_1—
I_2-(789)



B.P. 147–150° at 760 mm.	**(1)**	D_4^{23} **= 1.1404 (4)**	n_D^{23} **= 1.478 (4)**
147–149°	**(2)**		
147°	**(3)**	D_4^{15} **= 1.1422 (4)**	
146–148°	**(4)**		
53–54° at 20 mm.	**(4) (5)**	D_4^{0} **= 1.1590 (4)**	

Colorless lachrymatory liq. gradually becoming colored in light. — Spar. sol. aq.; eas. sol. alc., ether, $CHCl_3$. — Volatile with steam. — Note that although two geometrical isomers are possible only this one (configuration uncertain) is known.

3:8152 TETRAHYDRO-α-FURFURYL CHLORIDE C_5H_9OCl Beil. S.N. 2362
(2-(Chloromethyl)tetrahydrofuran)



B.P. 150–151°	at 762 mm. (1)	D_4^{20} = 1.1102 (2)	n_D^{20} = 1.4560 (2)
149.0–149.5°	at 721 mm. (2)		
47–48°	at 15 mm. (3)		n_D^{12} = 1.45922 (1)
41–42°	at 11 mm. (3)		
38.5–39°	at 10 mm. (2)		

Water-white liq. with mild and pleasant odor. — C̄ has no lachrymatory properties and is relatively stable (2); its chlorine atom is extremely unreactive (2).

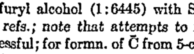
[For prepn. of C̄ from tetrahydro-α-furfuryl alcohol (1:6445) with $SOCl_2$ + pyridine *(yields: 75% (2), 73–75% (3)) see indic. refs.; note that attempts to replace $SOCl_2$ by* PCl_3 (excess) in dry ether (2) were *not* successful; for formn. of C̄ from 5-chloropentanediol-1,4 (1) by dehydrative ring closure with 15% H_2SO_4 at 100° for 2 hrs. (19% yield) see (1).]

C̄ with metallic Na in dry ether under reflux, subsequently decomposed by water, gives (yields: 82% (4), 76–83% (3)) penten-4-ol-1 (penten-1-ol-5) [Beil. I-443, I₂-(483)], b.p. 141.0–141.5° at 758 mm. (5), 139° at 760 mm. (6), 138.8–139.3° at 760 mm. (7); D_4^{25} = 0.8588 (7), D_4^{20} = 0.8457 (5); n_D^{20} = 1.43085 (5), $n_D^{15.5}$ = 1.4312 (8), n_D^{15} = 1.4305 (9) (corresp. allophanate, m.p. 148° (6), 147–148° (9); corresp. *N*-phenylcarbamate, oil, b.p. 183.5° at 16 mm. (8)).

C̄ with thiourea refluxed in alc. 4 days gives (10) *S*-(tetrahydro-α-furfuryl)isothiourea, isolated as corresp. picrate, m.p. 153.0–153.5° (10).

3:8152 (1) Paul, *Ann. chim.* (10) **18**, 385–386 (1932). (2) Kirner, *J. Am. Chem. Soc.* **52**, 3251–3255 (1930). (3) Brooks, Snyder, *Org. Syntheses* **25**, 84–86 (1945). (4) Gaubert, Linstead, Rydon, *J. Chem. Soc.* **1937**, 1972. (5) Juvala, *Ber.* **63**, 1993 (1930). (6) Paul, *Compt. rend.* **195**, 1290–1291 (1932). (7) Ginnings, Herring, Coltrane, *J. Am. Chem. Soc.* **61**, 807 (1939). (8) Robinson, Smith, *J. Chem. Soc.* **1936**, 196. (9) Paul, *Compt. rend.* **192**, 1574 (1931). (10) Sprague, Johnson, *J. Am. Chem. Soc.* **59**, 2440–2441 (1937).

3:8153 5-CHLORO-2,3-DIMETHYLPENTANE $C_7H_{15}Cl$ Beil. S.N. 10
(1-Chloro-3,4-dimethylpentane)



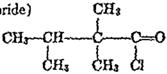
B.P. 150–151°	at 745 mm. (1)	D_4^{20} = 0.8825 (1)	n_D^{20} = 1.4299 (1)
52–53°	at 20 mm. (1)		

[For prepn. of C̄ from allyl chloride (3:7035) with 2-methylpropane (isobutane) + $AlCl_3$ at −10° (35–40% yield accompanied by 13–15% yield 4,5-dichloro-2,2-dimethylpentane (3:8516) see (1).]

C̄ on hydrolysis with aq. MgO in s.t. at 225° for 4 hrs. gives (54% yield (1)) 3,4-dimethylpentanol-1, b.p. 168–169°, n_D^{20} = 1.4288 (corresp. 3,5-dinitrobenzoate, m.p. 51–52°; corresp. *N*-(α-naphthylcarbamate), m.p. 41–42°) (1).

C̄ with Mg in dry ether gives corresp. RMgCl cpd.; this prod. on hydrolysis with aq. $(NH_4)_2SO_4$ gives (54% yield (1)) 2,3-dimethylpentane (1:8554) or on oxidn. with air gives (62% yield (1)) 3,4-dimethylpentanol-1 (see preceding paragraph); see also below.

3:8145 α,α,β-**TRIMETHYL-*n*-BUTYRYL CHLORIDE** $C_7H_{13}OCl$ Beil. S.N. 162
(Dimethyl-isopropyl-acetyl chloride)



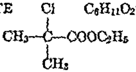
B.P. 148–150° (1)

[For prepn. of C̄ from dimethyl-isopropyl-acetic acid [Beil. II-346, II_1-(147)] see (1).]
C̄ on hydrolysis yields dimethyl-isopropyl-acetic acid (see above), camphoraceous cryst. from pet. ether, m.p. 50° (2) (3), 41–42° (1).

Ⓓ Dimethyl-isopropyl-acet-amide: m.p. 133–134° (2), 129° (1).

3:8145 (1) Locquin, Leers, *Compt. rend* **179**, 55 (1924). (2) Haller, Bauer, *Compt. rend.* **149**, 6 (1909). (3) Richard, *Ann. chim.* (8) **21**, 353 (1910).

3:8147 ETHYL α-CHLORO-ISOBUTYRATE $C_6H_{11}O_2Cl$ Beil. II-295
II_1—
II_2—

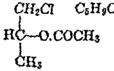


B.P. 148.5–149° cor. (1) $D_-^0 = 1.062$ (1) $n_D^{15} = 1.4109$ (5)
148–149° (2)
147–148.5° at 760 mm. (5)

[For prepn. of C̄ from α-chloro-isobutyric acid (3:0235) with EtOH + HCl see (3); from α-chloro-isobutyryl chloride (3:5385) with EtOH see (2).]
[C̄ on htg. with 1–5% $FeCl_3$ at 100° or above loses HCl yielding (4) ethyl methacrylate, b.p. 118–119° (4).]

3:8147 (1) Balbiano, *Ber* **11**, 1093 (1878). (2) Henry, *Rec. trav. chim* **26**, 84–85 (1907); *Compt. rend.* **142**, 1023 (1906), *Bull. acad. roy Belg.* **1906**, 206–226; *Cent* **1906**, II 227. (3) Balbiano, *Gazz. chim. ital* **8**, 372 (1878). (4) Barrett (to du Pont), U.S. 2,013,648, Sept. 10, 1935; *Cent.* **1936**, I 3217; *C A.* **29**, 6902 (1935). (5) Kahovec, Kohlrausch, *Monatsh* **74**, 116 (1943).

3:8150 β-**CHLOROISOPROPYL ACETATE** $C_5H_9O_2Cl$ Beil. II-130
(2-Acetoxy-1-chloropropane) II_1—
II_2—



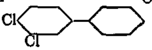
B.P. 149–150° (1) (2) $D_-^{20} = 1.0788$ (3) $n_D^{20} = 1.4223$ (3)
147–149° at 745 mm. (3)

[For prepn. (72% yield (3)) from propylene + *ter*-butyl hypochlorite (3:7165) + AcOH see (3); for prepn. from 1-chloropropanol-2 (3:7747) + AcCl see (2); for formn. from 1,2-diacetoxypropane + HCl gas see (4).]
1 ml aq. dis. 8 ml. C̄. — With $N/10$ HCl at 35° or 45° C̄ hydrolyzes much more slowly than isopropyl acetate (1.3041), but no chloride ion is liberated at 35° (1).

Ⓓ 1-Phthalimido-2-acetoxypropane [Beil. XXI_1-(369)]. from C̄ on htg. 2 hrs. with K phthalimide; m.p. 99–100° (5).

3:8150 (1) Henry, *Cent* **1902**, II 1093. (2) Bancroft, *J. Am. Chem. Soc.* **41**, 427 (1919). (3) Irwin, Hennion, *J. Am. Chem. Soc.* **63**, 859 (1941). (4) Dewael, *Bull. soc. chim. Belg.* **39**, 400 (1930). (5) Gabriel, Ohle, *Ber.* **50**, 808 (1917).

3:0685 2,4-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ Beil. V —
V₁—
V₂-(483)



M.P. 46° (1) B.P. 195–200° at 15 mm. (1)
49–50° (2)

Pale yel. cryst. (1).

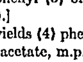
[For prepn. of Č from 3-amino-4-chlorobiphenyl (3) or from 4-amino-3-chlorobiphenyl (1) via appropriate diazo methods see (1) (3).]

Č htd. with aq. alk. for 3 hrs. at 290–300° yields (4) phenylpyrocatechol (3,4-dihydroxybiphenyl) (1:1576), m.p. 144.8–145.2° (4); diacetate, m.p. 77.5–78° (4).

Č on oxidn. with CrO_3 + AcOH yields (1) (3) 3,4-dichlorobenzoic acid (3:4925), m.p. 198° (3), 200° (1).

3:0685 (1) Scarborough, Waters, *J. Chem. Soc.* **1926**, 560. (2) Zerweck, Schütz (to General Aniline and Film Corp.), U.S. 2,280,504, Apr. 21, 1942; *C.A.* **36**, 5658 (1942). (3) Blakey, Scarborough, *J. Chem. Soc.* **1927**, 3007. (4) Harvey (to E. R. Squibb and Sons), U.S. 1,952,755, March 27, 1934; *Cent.* **1934**, II 1846; *C.A.* 28, 3426 (1934).

3:0700 6-CHLORO-3-METHYLPHENOL C_7H_7OCl Beil. VI —
(2-Chloro-5-methylphenol; VI₁-(187)
6-chloro-*m*-cresol) VI₂-(355)



M.P. 46° (1) (3) (2) B.P. 197–198° (1) $D^{15}_{-} = 1.215$ (5)
45° (4) 196° at 760 mm. (5) (3)
85° at 15 mm. (2)

Strong camphoraceous odor! — Cryst. from ice-cold lt. pet. ether (3) (2). — Volatile with steam (2).

[For prepn. from 4-chloro-3-aminotoluene (2-chloro-5-methylaniline) [Beil. XII-871] via diazo reaction see (1) (2) (4); from 6-amino-*m*-cresol (2-amino-5-methylphenol) [Beil. XIII-590] see (1).]

Č treated with $(CH_3)_2SO_4$ + aq. NaOH gives its methyl ether, 2-chloro-5-methylanisole, b.p. 212.5° (3). [This methyl ether on oxidn. with dil. $KMnO_4$ (2.7 hrs. for 5 g.) gave (3) 4-chloro-3-methoxybenzoic ac., pr. from 50% alc. or pl. from $CHCl_3$, m.p. 211° (3), Neut. Eq. 186.5.]

Ⓓ 6-Chloro-3-methylphenyl benzoate: from Č + BzCl + pyridine; pr. contg. alc. (3) from alc., m.p. 31° (3), 38° (1); cryst. from lt. pet. ether, m.p. 40° (3).

Ⓓ 6-Chloro-3-methylphenyl benzenesulfonate: from Č + benzenesulfonyl chloride + pyridine; cryst. from alc., m.p. 99° (1).

Ⓓ 6-Chloro-3-methylphenyl *p*-toluenesulfonate: from Č + *p*-toluenesulfonyl chloride + pyridine; hexag. pr. from alc. (3) (1) or acetone (3), m.p. 96° (3), 93–94° (1).

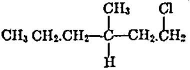
3:0700 (1) Houston, Chen, *J. Am. Chem. Soc.* **55**, 4214–4216 (1933). (2) Kraay, *Rec. trav. chim.* **49**, 1090 (1930). (3) Gibson, *J. Chem. Soc.* **1926**, 1424–1425. (4) Hodgson, Moore, *J. Chem. Soc.* **1926**, 2038–2039. (5) Raschig, Ger. 232,071, March 4, 1911; *Cent.* **1911**, I 854.

Ⓓ γ,δ-Dimethylcaproanilide: nacreous flakes from dil. alc., m.p. 80–81° (1). [From C̄ by conversion to RMgCl and reaction with phenyl isocyanate (1) according to method of (2) cf. (3).]

3:8153 (1) Schmerling, *J. Am. Chem. Soc.* **67**, 1438–1441 (1945). (2) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1063–1068 (1931). (3) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117–2120 (1934).

3:8155 *d,l*-1-CHLORO-3-METHYLHEXANE

$C_7H_{15}Cl$ Beil. I — I_1— I_2-(119)



B.P. 150–152° at 758 mm. (1) D_4^{20} = 0.8766 (1) n_D^{20} = 1.4274 (1)

[For prepn. of C̄ from 3-methylhexanol-1 [Beil. I_2-(445)] with alc. HCl in s.t. at 100° see (1).] [The dextrorotatory form of C̄ has also been prepd. (2) from levorotatory 3-methylhexanol-1 with $SOCl_2$; b.p. 66° at 25 mm.; D_4^{29} = 0.854; n_D^{30} = 1.4282 (2).]

3:8155 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* **33**, 498 (1924). (2) Levene, Marker, *J. Biol. Chem.* **91**, 90 (1931).

3:8160 ISOPROPYL CHLOROACETATE

$C_5H_9O_2Cl$ Beil. II - 198 II_1— II_2-(192)

$(CH_3)_2CH.O.CO.CH_2Cl$

B.P. 150.4–151.6°	(1)	D_4^{25} = 1.0812 (3)	n_D^{25} = 1.4175 (3)
149.5° at 760 mm.	(2)	D_4^{20} = 1.0888 (5)	n_D^{20} = 1.4192 (5)
149.5° at 747 mm.	(3)	D_4^{15} = 1.0944 (4)	
149–150° at 760 mm.	(4)		

Oil with agreeable odor; insol aq., sol. alc., ether.

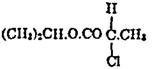
[For prepn. (38.8% yield (3)) from isopropyl alc. (1:6135) + chloroacetic ac. (3:1370) see (3) (4); for prepn. (34.2% yield (3)) from propylene + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of C̄ see (2).]

3:8160 (1) Cheng, *Z. physik. Chem.* **B-24**, 309 (1934). (2) Roark, Cotton, *Ind. Eng. Chem.* **20**, 512–514 (1928). (3) Dorris, Sowa, Nieuwland, *J. Am. Chem. Soc.* **56**, 2689–2690 (1934). (4) Steinlen, *Bull. acad. roy Belg.* (3) **34**, 101–108 (1897), *Cent* **1897**, II 659. (5) Schjanberg, *Z. physik. Chem* **A-172**, 228 (1935).

3:8165 ISOPROPYL *d,l*-α-CHLOROPROPIONATE

$C_6H_{11}O_2Cl$ Beil. S.N. 162

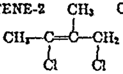


B.P. 151.5–152.5° at 760 mm. (1) D_4^{20} = 1.0315 (2) n_D^{20} = 1.4149 (2)

46.1–46.9° at 12 mm. (1)

3:8165 (1) Burkard, Kahovec, *Monatsh.* **71**, 340 (1938). (2) Schjanberg, *Z. physik. Chem.* **A-172**, 230 (1935).

3:8170 1,3-DICHLORO-2-METHYLBUTENE-2 $C_5H_8Cl_2$ Beil. S.N. 11



B.P. 151–153° (1) D_4^{19} = **1.1276 (1)** n_C^{19} = **1.4737 (1)**

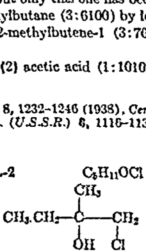
Two geom. stereoisomers of Č are possible, but only this one has been reported.

[For formn. of Č from 1,2,3-trichloro-2-methylbutane (3:6100) by loss of 1 HCl through distn. over KOH see (2); from 3,3-dichloro-2-methylbutene-1 (3:7690) by htg. (allylic transposition) see (1).]

Č on oxidn. with $KMnO_4$ in acetone gives (2) acetic acid (1:1010) and methylglyoxal [Beil. I-762, I_1-(395), I_2-(819)].

3:8170 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938), *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939). (2) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936); *Cent.* **1937**, I 573, *C.A.* **31**, 1003 (1937).

3:8175 1-CHLORO-2-METHYLBUTANOL-2 $C_5H_{11}OCl$ Beil. I - 389
(*unsym.*-Ethyl-methyl-ethylene chlorohydrin; chloromethyl-ethyl-methyl-carbinol) I_1-(196) I_2-(424)



B.P. 152–153° (1) D_-^0 = **1.068 (1)**
145–149° (2)

[For prepn. of Č from chloroacetone (3:5425) with EtMgBr see (1) (2) (3) (4) (5); note that in this reactn. Č is accompanied by 3-methylhexanol-4 [Beil I-416], whose b.p. (150°) is so close to that of Č that separation by distillation is impossible.]

Č on distillation (5) or on treatment with Ac_2O + conc. H_2SO_4 (5) yields 1-chloro-2-methylbutene-1 (3:7303) and 1-chloro-2-methylbutene-2 (3:7485); Č on distn. over anhydrous oxalic acid (1:0535) yields (6) both these halo-olefins and also 2-(chloromethyl)-butene-1 (3:9214). [Č on distn. over anhydrous oxalic acid (1:0535) and passing the resultant vapors over soda-lime or burnt lime at 600° yields (7) 2-methylbutadiene-1,3 (isoprene) (1:8020).]

Č with PCl_5 yields (5) 1-chloro-2-methylbutene-1 (3:7303).

Č with conc. aq. NaOH at 40–50° gives (63% yield (9) (1) (4) (10) 1,2-epoxy-2-methylbutane (*unsym*-ethyl-methyl-ethylene oxide) [Beil. XVII-13, $XVII_1$-(8)], b p. 82°.

3:8175 (1) Fourneau, Tiffeneau, *Compt. rend.* **145**, 437–438 (1907). (2) Tiffeneau, *Compt. rend.* **134**, 774 (1902). (3) Bruylants, *Bull. acad roy Belg.* (5) **17**, 1008–1020 (1931). (4) Kyriakides, *J. Am. Chem. Soc.* **36**, 657–663 (1914). (5) Seyer, Chalmers, *Trans. Roy. Soc. Can.* (3) **20**, III 337 (1926); *Cent.* **1927**, II 1811; *C.A.* **21**, 2663 (1927). (6) Chalmers, *Trans. Roy Soc. Can.* (3) **22**, III 75–76 (1928), *Cent.* **1929**, I 632; *C.A.* **23**, 2691 (1929). (7) Harries, *Ann.* **383**, 178 (1911). (8) Harries, Ger 243,075 + 243,076, Jan. 31, 1912; *Cent.* **1912**, I 535. (9) Fourneau, Benoit, Firmenick, *Bull soc. chim.* (4) **47**, 870 (1930). (10) Riedel, Ger. 199,148, June 3, 1908; *Cent.* **1908**, II 121.

3:8180 β-CHLORO-n-PROPYL ACETATE (1-Acetoxy-2-chloropropane) $C_5H_9O_2Cl$ Beil. II - 129, II_1-(58), II_2—

$$CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle H}{C}}-CH_2.O.CO.CH_3$$

B.P. 152–153° at 760 mm. (1) $D_4^{20} = 1.095$ (2); $n_D^{20} = 1.42213$ (2)
151–152° at 768 mm. (2) $D_{20}^{20} = 1.098$ (3)

Colorless oil with agreeable odor. — Insol aq.

[Note that $\bar{C}$ has never been obtd. in authentically pure state. The prepn. of Henry (1) was later shown (4) to be actually a mixt. of $\bar{C}$ with 2-acetoxy-1-chloropropane (3:8150); that of Dewael (2) was admittedly such a mixture.]

Henry's material was obtd. from 1-chloropropanol-2 by treatment with KOAc and conversion of the presumably resultant 1-acetoxypropanol-2 with $SOCl_2$ to $\bar{C}$; Dewael's material was obtd. from 1,2-diacetoxypropane by treatment with HCl gas.

3:8180 (1) Henry, *Cent.* 1902, II 929, 1093. (2) Dewael, *Bull. soc. chim. Belg.* 39, 400 (1930). (3) Henry, *Cent.* 1903, II 486. (4) Gabriel, Ohle, *Ber.* 50, 806 (1917).

3:8185 4-CHLORO-OCTENE-2 (α-(n-Butyl)crotyl chloride) $C_8H_{15}Cl$ Beil. S.N. 11

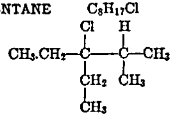
$$CH_3.CH_2.CH_2.CH_2-\overset{\displaystyle Cl}{CH}.CH{=}CH.CH_3$$

B.P. 153° (1) $D_4^{20} = 0.8924$ (2) $n_D^{25} = 1.4590$ (1)
69–70° at 9 mm. (2) 0.8816 (1) $n_D^{20} = 1.4452$ (2)

Note that two geom. stereoisomers of $\bar{C}$ are possible; also the possibility that by allylic transposition $\bar{C}$ may react in the form of its as yet unrecognized synionic isomer, 2-chloro-octene-3.

3:8210 3-CHLORO-3-ETHYL-2-METHYLPENTANE $C_8H_{17}Cl$ Beil. I-164

(3-Chloro-3-methoethylpentane; diethyl-isopropyl-carbinyl chloride) I_1— I_2—



B.P. 150–155° dec. (1).

[For prepn. from 3-ethyl-2-methylpentanol-3 (diethyl-isopropyl-carbinol) [Beil. I-423, I_2-(454)] with PCl_5 see (1).]

3:8210 (1) Grigorowitsch, Pavlov, *J. Russ. Phys.-Chem. Soc.* **23**, 169 (1891).

3:8215 ISOAMYL CHLOROFORMATE $C_6H_{11}O_2Cl$ Beil. III-12

(Isoamyl chlorocarbonate) iso-$C_5H_{11}O.CO.Cl$ III_1-(6) III_2-(11)

B.P. 154.3° cor. (1) D_4^{15} = **1.0321 (2)** n_{He}^{15} = **1.41916 (2)**

[For prepn. from isoamyl alc. (1:6200) + phosgene (3:5000) see (1).]

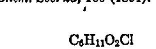
Ⓓ Isoamyl carbamate: m.p. 64.5° (3), 59° (4). [This deriv. is not recorded directly from C̄ but should be preparable by actn. of conc. aq. NH_4OH cf. (5).]

Ⓓ Isoamyl *N*-phenylcarbamate (isoamyl carbanilate): m.p. 57–58° (6), 57–59° (7), 55° (8), 55–56° (9). [This deriv. is not recorded directly from C̄ but should be preparable by actn. of aniline, cf. (5).]

3:8215 (1) Roese, *Ann.* **205**, 230 (1880). (2) von Auwers, *Ber.* **60**, 2140 (1927). (3) Marckwald, *Ber.* **37**, 1040 (1904). (4) Béhal, *Bull. soc. chim.* (4) **25**, 480 (1919). (5) Chattaway, Saerens, *J. Chem Soc.* **117**, 708–711 (1920). (6) Locquin, *Bull. soc. chim.* (3) **31**, 600 (1904). (7) Levene, Allen, *J. Biol Chem.* **27**, 440 (1916). (8) Marckwald, *Ber.* **37**, 1049 (1904). (9) Nekrassow, Melnikow, *J. prakt. Chem.* (2) **126**, 92 (1930).

3:8217 1-CHLOROPENTANONE-2 C_5H_9OCl Beil. I—

(Chloromethyl *n*-propyl ketone) I_1-(350) I_2-(738)



B.P. 154.5–156° sl. dec. (1)
58–59° at 17 mm. (1)
55–57° at 15 mm. (2)

Liquid with penetrating odor. — Very spar. sol. aq.; volatile with steam.

[For prepn. of C̄ from 1-chloropentanol-2 (3:8225) by oxidn. with $K_2Cr_2O_7/H_2SO_4$ see (2); from 2-chloromethyl-4-methyl-2-propyl-1,3-dioxolone-5 [Beil. XIX_1-(657)] by hydrolytic cleavage with alk., or from 2-chloromethyl-4,4-dimethyl-2-propyl-1,3-dioxolone-5 [Beil. XIX_1-(657)] by hydrolytic cleavage with aq. HCl/AcOH on warming (75–80% yield), see (1).]

[C̄ with dry K formate in MeOH refluxed overnight yields (2) pentanone-2-ol-1 [Beil. I_2-(872)], b.p. 62–64° at 18 mm. (2), 54–56° at 11 mm., D_4^{20} = 0.9860, n_D^{20} = 1.4234 (3).]

C̄ readily forms a cpd. with satd. aq. $NaHSO_3$ soln. (2).

C̄ does *not* react (4) with benzenediazonium hydroxide (diazotized aniline in NaOAc soln), cf. chloroacetone (3:5425).

Ⓓ **1-Chloropentanone-2 semicarbazone:** m.p. 157° (instantaneous fusion on Hg bath) *with decomp.* (1).

3:8217 (1) Blaise, *Bull. soc. chim.* (4) **15**, 672–673 (1914); *Compt. rend.* **155**, 48 (1912). (2) Levene, Haller, *J. Biol. Chem.* **77**, 560–561 (1928). (3) Schmidt, Ascherl, *Ber.* **58**, 358 (1925). (4) Favrel, *Bull. soc. chim.* (5) **1**, 990 (1934).

3:8219 1-CHLOROHEPTENE-1 $CH_3.(CH_2)_4.CH{=}CHCl$ $C_7H_{13}Cl$ Beil. I - 219 I_1— I_2-(196)

B.P.	*155°* cor.	(1)
	149–150° at 733 mm.	(2)
	148°	(3)
	78–82° at 75 mm.	(4)

Note that although two geom. steroisomers of C̄ are possible only one has yet been recognized.

[For prepn. of C̄ from 1,1-dichloroheptane (3:8650) by elimination of 1 HCl with alc. KOH (1) (3) (note, however, that yields are low (4) and the process has sometimes (5) failed), or better large excess solid KOH at 200° (62% yield (4)), see indic. refs.; from *n*-heptaldehyde (1:0183) with PCl_5 see (6).]

C̄ with KOH in mineral oil at 250° (4), or with $NaNH_2$ in toluene or xylene at 100–150° (6), or in mineral oil (Nujol) at 150–155° (7) gives (yields: 54% (7), 37% (4)) heptyne-1 (1:8085), b.p. 98°.

[C̄ with perbenzoic acid (benzoyl hydrogen peroxide) in $CHCl_3$ for 25 days gives (2) corresp. oxide, viz., 1-chloro-1,2-epoxyheptane, b.p. 93–95° at 50 mm., $D_4^{16} = 0.9874$, $n_D = 1.4370$ (2).]

[C̄ with $NaSC_2H_5$ in *n*-BuOH under reflux or better in EtOH at 138° under pressure gives (8) ethyl hepten-1-yl sulfide, b.p. 196–202°.]

3:8219 (1) Limpricht, *Ann.* [illegible] (3) Welt, *Ber.* **30**, 1496 (1897). [illegible] Guest *J. Am. Chem. Soc.* **47**, 861 (19[illegible] 1924). (7) Johnson, McEwen, *J. Am. Chem. Soc.* **48**, 473 (1926). (8) Loevenich, Losen, Dierichs, *Ber.* **60**, 954 (1927).

3:8220 *ter*-BUTYL CHLOROACETATE $C_6H_{11}O_2Cl$ Beil. S.N. 160

$(CH_3)_3C.O.CO.CH_2Cl$

B.P.	**155°** sl. dec.	(1)	$n_D^{20} = $ **1.4260** (2)
	60.2° at 15 mm.	(1)	**1.4230** (1)
	48–49° at 11 mm.	(2)	

Colorless liq. heavier than aq. (1).

[For prepn. (yield: 63% (2), 60% (1)) from *ter*-butyl alc. (1:6140) + chloroacetyl chloride (3:5235) + dimethylaniline see (1) (2).]

Hydrolysis yields (1) *ter*-butyl alc. (1:6140) + chloroacetic acid (3:1370) (1); Sap. Eq. = 150 5 (1).

3:8220 (1) Westheimer, Shookhoff, *J. Am. Chem. Soc.* **62**, 271 (1940). (2) Baker, *Org. Syntheses* **24**, 21 (1944).

3:8223 3-CHLORO-3-ETHYLHEXANE $C_8H_{17}Cl$ Beil. I - 162
(Diethyl-*n*-propyl-carbinyl chloride) I_1—
I_2-(126)

$CH_3.CH_2.CH_2—C(Cl)(C_2H_5)—CH_2.CH_3$

B.P. 155° sl. dec. (1)

[For prepn. of Č from 3-ethylhexanol-3 (diethyl-*n*-propyl-carbinol) [Beil. I-421, I_1-(210), I_2-(454)] with PCl_5 see (1).]
[Č with diethylamine loses HCl (2) yielding an olefin (2).]
[For data on density and parachor of Č at 0°, 15°, 25°, 50°, and 65° see (3).]

3:8223 (1) Butlerow, *Bull. soc. chim.* (2) **5**, 23 (1866). (2) Montagne, *Ann. chim.* (10) **13**, 111 (1930). (3) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3107–3111 (1939).

3:8224 METHYL *d,l*-β-CHLORO-*n*-BUTYRATE $C_5H_9O_2Cl$ Beil. II - 277
II_1—
II_2—

$CH_3.CH(Cl).CH_2.COOCH_3$

B.P. 155–156° at 750 mm. (1) $D_4^{20} = 1.0996$ (2) $n_D^{20} = 1.4258$ (2)

[For prepn. of Č from methyl crotonate (1:3121) by addn. of HCl, from β-chloro-*n*-butyronitrile + MeOH + HCl, or from methyl *n*-butyrate (1:3080) with Cl_2 see (1).]
Č on hydrolysis yields MeOH (1:6120), crotonic acid (1:0425), and HCl.

3:8224 (1) Henry, *Bull. acad. roy. Belg.* (3) **35**, 507–520 (1898); *Cent.* **1898**, II 273. (2) Schjanberg, *Z. physik. Chem.* **A-172**, 232 (1935).

3:8225 *d,l*-1-CHLOROPENTANOL-2 $C_5H_{11}OCl$ Beil. I —
(Chloromethyl-*n*-propyl-carbinol; *n*-propylethylene chlorohydrin) I_1—
I_2-(419)

$CH_3.CH_2.CH_2—CH(OH)—CH_2Cl$

B.P. 157–160° at 735 mm. (1)		$D_{25}^{25} = 1.0143$ (1)	$n_D^{25} = 1.4404$ (1)
68–75° at 30 mm. (2)			
66–67° at 18 mm. (3)		$D_{20}^{20} = 1.037$ (2)	$n_D^{20} = 1.4520$ (2)
59–62° at 14 mm. (4)		1.031 (3)	1.4422 (3)

[For prepn. of Č from pentene-1 (1:8205) with HOCl (43% yield) see (2); from 1-chloro-2,3-epoxypropane (epichlorohydrin) (3:5358) with $MgEt_2$ (70% yield (3)) or with EtMgBr (16–19% yield (1)) see indic. refs.; from chloroacetaldehyde (3:7212) with *n*-PrMgBr see (4).]
Č with AcCl yields (1) 1-chloro-2-acetoxypentane, b.p. 186–188° at 740 mm., D_{25}^{25} = 1.0825, n_D^{25} = 1.4328 (1); Č with NaSMe gives (45% yield (2)) 1-methylthiolpentanol-2, b.p. 90° at 18 mm., D_{20}^{20} = 0.943, n_D^{20} = 1.4792 (2); Č with $SOCl_2$ + diethylaniline gives (70% yield (1)) 1,2-dichloropentane (3:8140); Č with 2 moles EtMgBr yields (3) heptanol-4 (1:6228).
Č on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ yields (4) 1-chloropentanone-2 (3:8217), b.p. 55–57° at 15 mm. (4); Č on oxidn. with aq. $KMnO_4$ yields (1) *n*-butyric acid (1:1035) q.v.

① **Chloromethyl-*n*-propyl-carbinyl 3,5-dinitrobenzoate**: pl. from alc., m.p. 84–85° (3), 83–84° (1), from Č on htg. with 3,5-dinitrobenzoyl chloride until no more HCl is evolved (1).

3:8225 (1) Koelsch, McElvain, *J. Am. Chem. Soc.* **51**, 3392, 3393 (1929). (2) Glavis, Ryden, Marvel, *J. Am. Chem. Soc.* **59**, 709 (1937). (3) Magrane, Cottle, *J. Am. Chem. Soc.* **64**, 484–487 (1942). (4) Levene, Haller, *J. Biol. Chem.* **77**, 560 (1928).

3:8228 CHLOROACETALDEHYDE DIETHYLACETAL $C_6H_{13}O_2Cl$ Beil. I - 611
(Chloroacetal) CH_2—$CH(OC_2H_5)_2$ I_1-(328)
$\quad|$ I_2-(676)
$\;Cl$

B.P. 157.4°		(1)
157–158°		(11)
156.8° cor. at 756.8 mm.		(2)
156°		(13)
53–54°	at 16 mm.	(3)

D^{20}_{20} = **1.017** (3) n^{20}_{D} = **1.4171** (3)

[For prepn. from vinyl acetate (b.p. 69–71°) by treatment in abs. EtOH soln. with Cl_2 in dark and in a solid CO_2/acetone cooling bath (83% yield) see (3); from acetaldehyde diethylacetal ("acetal") (1:0156) with Cl_2 at 50° in presence of abs. alc. NaOEt (90% yield) see (4); from paraldehyde (1:0170) by chlorination and subsequent treatment *with EtOH see (5) (6); from EtOH (1:6130) by treatment with* Cl_2 see (7) (8).]

[For prepn. of C̄ from chloroacetaldehyde (3:7212) on warming with EtOH see (9); from chloroacetaldehyde ethyl alcoholate (chloroacetaldehyde ethyl-hemi-acetal) [Beil. I-611] in EtOH with dry HCl gas see (10); from α,β-dichloroethyl ethyl ether (3:5640) with 2 vols. abs. EtOH (2) or with NaOEt (11) (12) (13) see indic. refs.]

C̄ is comml. chem. in U.S. (1943) (14); C̄ is widely used in org. synthesis as source of combined chloroacetaldehyde (3:7212) and otherwise.

The acetal portion of C̄ is stable to alkali but readily hydrolyzed by aq. acids; the chlorine atom, however, behaves like a reactive alkyl halide; all these characteristics are illustrated in the reactns. cited below.

C̄ on warming with dil. H_2SO_4 yields (15) chloroacetaldehyde (3:7212) accompanied by some *bis*-(β-chloro-α-ethoxyethyl) ether, b.p. abt. 165°; C̄ on satn. at 100° with dry HCl gas yields (9) α,β-dichloroethyl ethyl ether (3:5640). — C̄ on htg. with AcOH at *120° or with anhydrous oxalic acid at 100–150° yields (12) chloroacetaldehyde (3:7212)* + ethyl acetate (1:3015) or diethyl oxalate (1:1055) respectively.

[C̄ htd. with NaOEt in s.t. at 140–150° for 30 hrs. (11) (13) (17) or with abs. alc. NaOEt at 160° under press. (16) gives (66% yield (16)) ethoxyacetaldehyde diethylacetal, b.p. 168° (11) (this prod. on boilg. with dil. H_2SO_4 (17) (13) (16) hydrolyzes to EtOH (1:6130) + ethoxyacetaldehyde (1:0159), b.p. 105–106°). — C̄ htd. with 10% excess of satd. abs. alc. KOH in s.t. for 75 hrs. gives (95% yield (18)) glycolaldehyde diethylacetal (hydroxyacetaldehyde diethylacetal) (1:0191), b.p. 167°.] [For reactn. of C̄ with many other alcs. (19) (20) and phenols (21) in pres. of alk. see indic. refs.]

[C̄ htd. with Na or Mg at *120–130°* (22) or with Na in ether at 0–20° (23) yields ethyl [illegible] ethoxyacetaldehyde diethylacetal [illegible]

[C̄ htd. with 4–5 vols. conc. aq. NH_4OH in s.t. at [illegible] for 12–14 hrs. (25) or C̄ [illegible] satd. alc. NH_3 in s.t. at 130° (26) (27) (28) or refluxed in pres. of NaI (29) yields aminoacetaldehyde diethylacetal [Beil. IV-308, IV_1-(449), IV_2-(758)], b.p. 163°. — C̄ htd. with alc. hydrazine hydrate under press. for 6 hrs. at 115–120° yields (30) hydrazinoacetaldehyde diethylacetal [Beil. IV-553].]

[C̄ with aniline + $NaNH_2$ in ether gives (77% yield (31)) *N*-(phenyl)aminoacetalde-

hyde diethylacetal [Beil. XII-213], b.p. 92–94° at 0 3 mm.; for corresp. behavior with benzylamine (32) or primary aliph. amines (33) see indic. refs.] — C̄ with 3 moles phenylhydrazine htd. several hrs. at 130° yields (34) glyoxal-*bis*-(phenylhydrazone), yel. tbls. from alc. or ether, m.p. 177° u.c., 179° cor. (34).

C̄ on acid hydrolysis (3) yields ethyl alcohol (1:6130) and chloroacetaldehyde (3:7212) q.v.

3:8228 (1) Lecat, *Rec. trav chim.* **45**, 622 (1926). (2) Paterno, Mazzara, *Gazz. chim. ital.* **3**, 254–256 (1873), *Ber.* **6**, 1202 (1873). (3) Filachione, *J. Am. Chem. Soc.* **61**, 1705–1706 (1939). (4) Anselm, Galitzenstein, Ger. 639,507, Dec. 7, 1936; *Cent.* **1937**, I 2023; *C.A.* **31**, 3940 (1927). (5) Freundler, *Bull. soc. chim.* (4) **1**, 70–71 (1907). (6) Soc des Usines Chimiques Rhone-Poulenc, French 711,095, Sept. 2, 1931; *Cent.* **1932**, I 130. (7) Lieben, *Ann.* **104**, 114–115 (1857). (8) Fritsch, *Ann.* **279**, 300 (1879). (9) Natterer, *Monatsh.* **5**, 497–499 (1884). (10) Fritsch, Schumacher, *Ann.* **279**, 308 (1894).

(11) Lieben, *Ann.* **146**, 193–201 (1868). (12) Natterer, *Monatsh.* **3**, 444–449 (1882). (13) Kluger, *Monatsh.* **26**, 880–882 (1905). (14) *Chem. Eng. News* **21**, [illegible] **206**, 341–344 (1880). (1[illegible] **27**, 1130–1132 (1906). ([illegible] Sabetay, *Bull. soc. chim.* ([illegible] 8, 129–136 (1933); *Cent.* 1[illegible]

(21) Parfumerie Houbigant, Sabetay, French 673,379, Feb. 14, 1930; *Cent.* **1930**, II 2694. (22) Wislicenus, *Ann.* **192**, 106–109 (1878). (23) Leuchs, Lemcke, *Ber.* **47**, 2577 (1914). (24) Späth, *Monatsh* **35**, 466–467 (1914). (25) Wolff, *Ber.* **21**, 1482 (1888); **26**, 1832 (1893). (26) Wolff, Marburg, *Ann.* **363**, 179–182 (1908). (27) Marckwald, *Ber.* **25**, 2355 (1892). (28) Buck, Wrenn, *J. Am. Chem. Soc.* **51**, 3613 (1929). (29) Wohl, *Ber.* **39**, 1953 (1906). (30) Fischer, Hunsalz, *Ber.* **27**, 178–179 (1894).

(31) Wohl, Lange, *Ber.* **40**, 4728 (1907). (32) Rügheimer, Schön, *Ber.* **41**, 17–18 (1908). (33) Paal, van Gember, *Arch. Pharm* **246**, 306–314 (1908). (34) Fischer, *Ber.* **26**, 97 (1893).

3:8230 4-CHLORO-OCTENE-4 $C_8H_{15}Cl$ Beil. S.N. 11

$$CH_3.CH_2\,CH_2.CH{=}\underset{|}{\overset{Cl}{C}}{-}CH_2.CH_2.CH_3$$

B.P. 157–159.5° at 750 mm. (1) **D_4^{25} = 0.8788 (1)** **n_D^{25} = 1.4394 (1)**

Although two geom. stereoisomers of C̄ are possible only this one has as yet been reported.

[For prepn of C̄ from octyne-4 (di-*n*-propylacetylene) (1·8110) with AcCl + $SnCl_4$ (both stereoisomers of 4-chloro-3-*n*-propylhepten-3-one-2 are also formed: *cis*, b.p. 117–118° at 28 mm., D_4^{25} = 0.9680, n_D^{25} = 1.4587; *trans*, b.p. 112–113° at 28 mm., D_4^{25} = 0.9592, n_D^{25} = 1.4601 (1)) see (1).]

3:8230 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163–169 (1936).

3:8235 *d,l*-α-ETHYL-*n*-VALERYL CHLORIDE $C_7H_{13}OCl$ Beil. II - 344

(*d,l*-2-Ethylpentanoyl chloride-1; ethyl-*n*-propyl-acetyl chloride)

$$CH_3.CH_2.CH_2.\underset{C_2H_5}{\underset{|}{CH}}\,.\,\underset{Cl}{\underset{|}{C}}{=}O$$

II₁—
II₂—

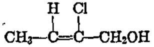
B.P. 158–160° (1)
50° at 11 mm. (2)

[For prepn. of C̄ from 2-ethylpentanoic acid-1 (ethyl-*n*-propyl-acetic acid) (1:1133) with PCl_3 (1) or $SOCl_2$ (2) see indic. refs.]

C̄ on hydrolysis yields ethyl-*n*-propyl-acetic acid (1:1133) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to C̄ see 1:1133).

3:8235 (1) Rasetti, *Bull. soc. chim.* (3) **33**, 687 (1905). (2) Reichstein, Trivelli, *Helv. Chim. Acta* **16**, 974 (1933); **15**, 258–259 (1932).

3:8240 2-CHLOROBUTEN-2-OL-1 (β-Chlorocrotonyl alcohol)



C_4H_7OCl Beil. I - 442, I_1—, I_2-(481)

B.P. 159° at 760 mm. (1)	$D_4^{23} = 1.0950$ (4)	$n_C^{23} = 1.45093$ (4)
158–161° (2)		
158.3° cor. at 742.5 mm. (3)	$D_4^{20} = 1.118$ (1)	$n_D^{20} = 1.46823$ (1)
52–53° at 19 mm. (4)		

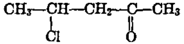
Note: *cis* and *trans* stereoisomers of $\bar{C}$ are theoretically possible but have not definitely been reported.

[For prepn. of $\bar{C}$ from 2-chlorobuten-2-al-1 (α-chlorocrotonaldehyde) (3:8117) by reduction in abs. alc. with H_2 + $Al(OEt)_3$ (2) or with $Mg(OEt)_2.EtOMgCl$ (1) see (2) (1); for formn. of $\bar{C}$ (together with 3-chlorobuten-3-ol-2) (3:9115) from either the low-boilg (3:5360) or high-boilg. (3:5615) stereoisomer of 1,2-dichlorobutene-2 by hydrolysis with 2 pts. aq. + 1 mole $CaCO_3$ for 4 hrs. at 70° see (4); for prepn. of $\bar{C}$ from 2,2,3-trichlorobutanol-1 (3:1336) with Zn dust + HCl see (3).]

Ⓓ 2-Chlorobuten-2-yl-1 *N*-(α-naphthyl)carbamate: m.p. 95–96° (4).

3:8240 (1) Meerwein et al., *J. prakt. Chem.* (2) **147**, 225 (1936). (2) I. G. Farbenindustrie, Ger. 437,160, Nov. 18, 1926; *Cent.* **1927**, I 802. (3) Garzarolli-Thurnlackh, *Ann.* **213**, 375–379 (1882). (4) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 658–662 (1937); *Cent.* **1937**, II 371–372; *C.A.* **31**, 5754 (1937).

3:8243 4-CHLOROPENTANONE-2 (β-Chloro-*n*-propyl methyl ketone)



C_5H_9OCl Beil. I - 678, I_1—, I_2—

B.P. 159–160° (1)

[For preparation of $\bar{C}$ from acetyl chloride (3:7065) + propylene in pres. of $ZnCl_2$ see (1); for reactn. of acetyl chloride with propylene in pres. of activated carbon at 100–300° and at press of 20–200 atm. cf. (2).]

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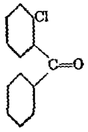
3:0715 2-CHLOROBENZOPHENONE (*o*-Chlorophenyl phenyl ketone)



$C_{13}H_9OCl$ Beil. VII - 419
VII_1-(227)

M.P. 46°	(1)	B.P. 330° (3) cor.	(4)
45.5–46°	(2)	185–188° at 13 mm.	(7)
45.5°	(3) (4) (5) (6) (8) (10)		
52–56°	(7)		

Tbls. from $CHCl_3$ + lgr. (3) (4); cryst. from pet. eth. (5). — [For crystallog. data see (5) (8).]

[For prepn. (93% yield (9)) from *o*-chlorobenzoyl chloride (3:6640) + C_6H_6 + $AlCl_3$ see (3) (5) (9); for formation (12%) in reaction of BzOH + chlorobenzene + $AlCl_3$ (main prod. 4-chlorobenzophenone (3:1914)) see (2).]

C̄ on reduction with 10% Na/Hg + alc. (11) or boilg. alc. KOH (12) gives almost exclusively 2-chlorodiphenylcarbinol [Beil. VI-680], m.p. 65° (11) (12), 62° (19). — C̄ with Al/Hg + 80% alc. (6) gives mainly 2-chlorodiphenylcarbinol (above) + a little 2,2'-dichlorobenzpinacol. — C̄ with Zn + AcOH (11) or C̄ in alc. on long exposure to sunlight (11) (13) (14) gives 2,2'-dichlorobenzpinacol [Beil. VI_1-(523)], m.p. 174–175° (6), 178° dec. (11).

C̄ htd. with aniline 3–4 hrs. at 200° yields (4) 2-chlorobenzophenone anil [Beil. XII-201], pale yel. ndls. or scales from alc., m.p. 128° (4). [Fused subst. or solns. in org. solvents (especially $CHCl_3$) are yellow.]

C̄ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) BzOH (1:0715) (90–95% yield) + chlorobenzene (3:7903) but no *o*-chlorobenzoic acid; however, C̄ with aq. NaOH + trace CuO in iron bomb (or in pres. of Fe powder) at 240° for 6 hrs. gives (58% yield (20)) fluorenone (1:9014).

C̄ with CH_3MgI yields (15) 1-(*o*-chlorophenyl)-1-phenylethylene, oil, b.p. 162–163° at 18 mm. (15); C̄ with Mg + MgI_2 easily loses nuclear halogen (16).

Ⓓ 2-Chlorobenzophenone oxime: from C̄ + $NH_2OH.HCl$ + dil. alc. KOH (5) (17) (7) or from C̄ + NH_2OH HCl + alc. htd. in s.t. for 3 hrs. at 130° (17); cryst. from pet. ether, m.p. 133–134° (17), 121° (5) (7). [With PCl_5 in dry ether, followed by aq. this oxime yields by Beckmann rearr. *o*-chlorobenzanilide [Beil. XII-266], m.p. 118° (5), 114° (17).] [The above oxime boiled with conc. aq. KOH for 1 day (5) or refluxed 6 hrs. with 20 pts. 30% MeOH/KOH, then diluted with aq. (17) (18), gives 3-phenylindoxazene [Beil. XXVII-71], ndls. or tbls. from ether or alc., m.p. 83–84° (18), 82.5° (5) (11).]

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(11) Ref. 10, pp. 157–160. (12) Montagne, van Charante, *Rec. trav. chim.* **31**, 311–312 (1912). (13) Cohen, Böeseken, *Rec. trav. chim.* **39**, 258 (1920). (14) Böeseken, Cohen, Langedijk, *Rec. trav. chim.* **46**, 383–396 (1927). (15) Bergmann, Bondi, *Ber.* **64**, 1473–1474 (1931). (16) Gom-

companying p-isomer (3:8287) varies widely, e.g., from 100% C̄ with $PbCl_2 + NH_4OH$ (42), through 62% o/28% p with $PbCl_2$ (8), to 2.5 o/1 p via the electrolytic methods (40) (for details the orig. refs. must be consulted).] — [For sepn. of C̄ from polychlorotoluenes via const.-boilg. mixt. with aq. see (79).]

[For prepn. of C̄ from hydrazone of o-chlorobenzaldehyde (3:6410) by Wolff-Kishner reduction (35–82% yield) see (113).]

[For thermal anal. of system: C̄ + $SbCl_3$ see (48).]

[C̄ with H_2 in pres. of $Pd/CaCO_3$ in alc./alk. soln. loses all its chlorine as HCl (49); C̄ with HI + P at 302° for 5 hrs. gives 80% yield (50) toluene (1:7405).]

C̄ on oxidn. with CrO_3 is completely destroyed (30); C̄ on oxidn. with boilg. aq. $KMnO_4$ (74–78% yield (51)) (52) (36) (53) or C̄ on cat. oxidn. with air over granular tin vanadate at 287° (13.8% yield (54)) cf. (55) or C̄ + KCN + $NiCl_2$ in dil. alc. 20 hrs. at 260–270° (7.5% yield (63)) gives o-chlorobenzoic acid (3:4150); C̄ with CrO_2Cl_2 followed by aq. (51.5% yield (56)) (57) or C̄ on oxidn. with Ce cpds. (58) or with air over Ta_2O_5 (59) cf. (60) or C̄ with $MnO_2 + H_2SO_4$ (61) or PbO_2 + dil. H_2SO_4 (24% yield (62)) gives o-chlorobenzaldehyde (3:6410).

[C̄ with Cl_2 in pres. of Al/Hg gives (64) a mixt. contg. 2,3- (3:6345), 2,4- (3:6290), 2,6- (3:6270), together with some 2,5-dichlorotoluene (3:6245). — C̄ with Cl_2 + 3% PCl_3 in light gives (65) (19) o-chlorobenzyl chloride (3:6400); C̄ with $Cl_2 + PCl_5$ at 150–180° (66) (67) (68) cf. (70) gives o-chlorobenzal (di)chloride (3:6625); C̄ with $Cl_2 + PCl_3$ (73) or with Cl_2 at 160–190° (69) gives (64% yield (69)) (70) (71) o-chlorobenzotrichloride (3:6880).]

[C̄ with Br_2 in pres. of Al/Hg in CCl_4 gives (74) mainly 5-bromo-2-chlorotoluene [Beil. V-307, V_1-(155)], together with a smaller amt. of 4-bromo-2-chlorotoluene [Beil. V-307, V_1-(155)]; the former is also obtd. (75) from C̄ + $Br_2 + HNO_3 + H_2SO_4$ in AcOH. — C̄ with Br_2 (76) (77) yields o-chlorobenzyl bromide [Beil. V_1-(155)] (for studies of rate of side-chain bromination of C̄ see (78)).]

[C̄ + $I_2 + HNO_3 + H_2SO_4$ in AcOH gives (75) 2-chloro-5-iodotoluene [Beil. V-315]]

[C̄ with $AlCl_3$ + HCl gas as directed (7) undergoes partial rearr. to both m-chlorotoluene (3:8275) and p-chlorotoluene (3:8287); for anal. of mixts. of the three isomers see (7).]

[C̄ with AcCl (80) or better Ac_2O (81) + $AlCl_3$ gives (70% yield (81)) 4-chloro-3-methylacetophenone [Beil. VII-307], b.p. 254.2–254.4° at 753.4 mm., n_D^{25} = 1.5521 (81). — C̄ with β-chloropropionyl chloride (3:5690) + $AlCl_3$ in CS_2 gives (68% yield (82)) (83) 2-chloro-5-(β-chloropropionyl)toluene, colorless pr. from C_6H_6, m.p. 46° (82), which on ring closure with conc. H_2SO_4 gives (82) (83) 6-chloro-7 (or 5)-methylindanone-1, cryst. from alc., m.p. 74–75° (82) (83). — C̄ with trichloroacetonitrile + $AlCl_3$ (4 moles) at 80–90° satd. with HCl gas for 2 days gives (40% yield (84)) 4-chloro-3-methyl-ω,ω,ω-trichloroacetophenone, b.p. 155–160° at 11 mm. (84). — C̄ with fumaryl (di)chloride + $AlCl_3$ in CS_2 at 50–60° for 2 hrs. gives (51% yield (85)) *trans-bis*-1,2-(4-chloro-3-methylbenzoyl) ethylene, pale yel. cryst. from alc., m.p. 167° (85).]

[C̄ with benzoyl chloride + $AlCl_3$ gives (83% yield (86)) 3-chloro-4-methylbenzophenone [Beil. VII_1-(236)], lfts. from alc., m.p. 82–83° (86); C̄ with o-chlorobenzoyl chloride (3:6640) + $AlCl_3$ in CS_2 for 12 hrs. gives (87) 2′,3-dichloro-4-methylbenzophenone, cryst. from alc., m.p. 43.5° (87). — C̄ with naphthalene-*bis*-1,4(or 5)-(dicarboxylic acid dichloride) + $AlCl_3$ gives (88) *bis*-1,4(or 5)(chlorotoluoyl)naphthalene (used for ring closure to corresp. dibenzpyrenequinones).]

[C̄ with phthalic anhydride + $AlCl_3$ at 90° gives (89) (90) (91) a mixt. (93% yield (90)) of two o-(chlorotoluoyl)benzoic acids A + B: A, m.p. 183–184° (90), 182–183° (91) (89), the main prod., is regarded variously as either (90) o-(3-chloro-4-methylbenzoyl)benzoic acid or (91) o-(4-chloro-3-methylbenzoyl)benzoic acid but in any case with conc. H_2SO_4

3:8245 o-CHLOROTOLUENE

C_7H_7Cl Beil. V - 290
V_1-(149)
V_2-(224)

B.P.			F.P.		
159.45–159.55°	at 760 mm.	(1)	−34.0°	(12)	D_4^{25} = 1.07762 (4)
159.5° cor.	at 759.5 mm.	(2)	−34.5°	(11)	n_D^{25} = 1.52221 (1)
159.38°	at 760.1 mm.	(3)	−34.7°	(13)	D_4^{20} = 1.08246 (4)
159.15°	at 760 mm.	(4)	−35.1°	(8)	1.08173 (14)
159.0–159.2° cor.		(5)	−36.5°	(4)	1.0785 (1)
158.93–158.97°	at 760 mm.	(6)		(10)	n_D^{20} = 1.52691 (4)
158.7–158.9°	at 754 mm.	(7)			D_4^{15} = 1.08729 (4)
158.4–158.7°	at 760.4 mm.	(8)			
158.3–159.3°		(9)			
157.2°	at 760 mm.	(10)			
147.7°	at 558.9 mm.	(3)			
142.3°	at 485.0 mm.	(3)			
134.2°	at 391.1 mm.	(3)			
123.3°	at 279.4 mm.	(3)			
112.1°	at 191.0 mm.	(3)			
95.2°	at 106.0 mm.	(3)			
93.2°	at 98.0 mm.	(3)			
41°	at 11 mm.	(11)			

[*See also p-chlorotoluene* (3:8287)]

[For f.p./compn. data on system. Č + *p*-chlorotoluene (3:8287) (eutectic, f.p. −50° conts. 73% Č) see (8) (112); for D_{20}^{20}/compn. data on this system see (8); for n_D^{19}/compn. data on this system see (15). — For f.p./compn. data on systems Č + chlorobenzene (3:7903) (13), Č + *m*-dichlorobenzene (3:5960) (16), Č + bromobenzene (16) see indic. refs.]

[For prepn. of Č from *o*-toluidine [Beil. XII-772, XII_1-(372)] via diazotization and use of Cu_2Cl_2 reactn. (yields. 85% (23), 79–90% (21), 74–79% (7), 70% (18)) (19) (20) (22), or Cu powder (66% yield (24)) (25), or mere boilg. with HCl (26), or use of CuH (27), or $CaCl_2$ (28) see indic. refs.; for prepn. from *o*-toluenediazonium chloride (solid) [Beil. XVI-495, XVI_1-(358)] with C_6H_6 + $AlCl_3$ (29), from *o*-toluenediazonium chloroplatinate on htg. (30), or from *o*-toluenediazopiperidide by htg with HCl (31) see indic. refs.; for prepn. of Č from *o*-cresol (1:1400) via conv. with PCl_5 at 140° to *tris*-(*o*-toloxy)phosphoric acid dichloride and htg of latter at 180° see (32); for prepn. of Č from *p*-toluenesulfonyl chloride via chlorination to 2-chlorotoluenesulfonyl chloride-4 followed by hydrolysis with 10% H_2SO_4 (33) to 2-chlorotoluenesulfonic acid-4 (see below) and subsequent replacement of $-SO_3H$ by H with superheated steam in 80% H_2SO_4 (overall yield 88–90% (33)) cf. (34) (35); for prepn. of Č from 2-chlorotoluenesulfonic acid-5 (see below) or its sodium salt by steam distn of its soln. in 75% H_2SO_4 see (8).]

[For prepn. of Č from toluene with Cl_2 in pres. of Fe (8) (36) (38), or I_2 (37) (39), Fe + I_2 (15), Al/Hg (45), $MoCl_5$ (36), $SbCl_5$ (39), or $PbCl_2$ (8), from toluene via electrolysis of its suspension in boilg HCl (40) or in HCl/AcOH at 35° (41), from toluene by boilg. with $PbCl_4.2NH_4Cl$ (42), from toluene with SO_2Cl_2 + cat. (43) especially $AlCl_3$ (43) (44), from toluene with n-butyl chlorosulfonate (46), from toluene with NCl_3 (47) see indic. refs.: no *m*-chlorotoluene is formed by any of these methods, but the proportion of Č to its ac-

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[illegible]

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ring-closes to give (92% yield (90)) (91) 2-chloro-3-methylanthraquinone, colorless tbls. from toluene, m.p. 219° (91) cor. (90); B, m.p. 176–177° (91), the minor prod., regarded (91) as *o*-(2-chloro-3-methylbenzoyl)benzoic acid, with conc. H_2SO_4 ring-closes to give 1-chloro-2-methylanthraquinone, yel.-br. ndls. from toluene, m.p. 171° (91), 170–171° (90).] — [For reactn. of $\bar{C}$ with 3,4-dichlorophthalic anhydride (3:3695) (92) or with pyromellitic anhydride (93) see indic. refs.]

[$\bar{C}$ with aq. NaOH in pres. of Cu at 350–360° under press. yields (94) a mixt. contg. 41% *o*-cresol (1:1400) + 59% *m*-cresol (1:1730) (for extensive study of hydrolysis of $\bar{C}$ as means of prepn of *m*-cresol (1:1730) see (112)); $\bar{C}$ with NH_3 + cat. under press. as directed (95) (96) (97) yields *o*-toluidine (for behavior of $\bar{C}$ with liquid NH_3 see (98)). — $\bar{C}$ with aniline + Cu at 175° yields (99) phenyl-*o*-tolylamine. — $\bar{C}$ with diphenylamine + K at 240–245° in H_2 gives (by rearr.) (100) *N,N*-diphenyl-*m*-toluidine, m.p. 69–70°.] — [Note that $\bar{C}$ does not react with aq. sodium sulfanilate + Na_2CO_3 (dif. from benzyl chloride (3:8535)) and use in sepn. of $\bar{C}$ from the latter (8).]

[$\bar{C}$ on mononitration, e.g., with 4 pts. HNO_3 ($D = 1.52$) at 0° (101) gives a mixt. contg all four possible isomers, viz., 43% 2-chloro-5-nitrotoluene [Beil. V-329, V_1-(163)], m.p. 42.9° (101), 44° (102), 21% 2-chloro-6-nitrotoluene [Beil. V-327, V_1-(162)], m.p. 35.3° (101), 37° (103) (104), 19% 2-chloro-3-nitrotoluene [Beil. V-328, V_1-(163)], m.p. 22.1° (101), 21.5° (105), and 17% 2-chloro-4-nitrotoluene [Beil. V-329, V_1-(163)], m.p. 62.3° (101), 65° (105A).]

$\bar{C}$ on dinitration, e.g., with mixt. of 3 wt. pts. HNO_3 ($D = 1.48$) + 9 wt. pts. conc H_2SO_4 at 100° (106), or with 2 vol. pts. HNO_3 ($D = 1.42$) + 5 vols. pts. conc. H_2SO_4 at 100° as directed (107), gives mainly (55–60% (107)) 2-chloro-3,5-dinitrotoluene [Beil. V-345, V_1-(169)], cryst. from alc., m.p. 64° (107), 63–64° (106), accompanied by smaller amts. of three isomers, viz., 2-chloro-4,5-dinitrotoluene, m.p. 88.5° (18–20% (107)), 2-chloro-5,6-dinitrotoluene, m.p. 106.5° (18–20% (107)), and 2-chloro-4,6-dinitrotoluene, m.p. 49° (1–2% (107)) [*the two other possible dinitro-2-chlorotoluenes have been prepd.* by indirect means, viz., 2-chloro-3,4-dinitrotoluene, m.p. 89° (108), and 2-chloro-3,6-dinitrotoluene, m.p. 62–63° (109)].

[$\bar{C}$ on monosulfonation with fumg. H_2SO_4 (37) or 100% H_2SO_4 (23) (8) or $ClSO_3H$ (110) (see below) yields 2-chlorotoluenesulfonic acid-5 [Beil. XI-95]; $\bar{C}$ sulfonates more readily (8) than *p*-chlorotoluene (3:8287) and may thus be used to separate $\bar{C}$ from the latter (8) (111).]

Ⓓ **2-Chlorotoluenesulfonamide-5 (4-chloro-3-methylbenzenesulfonamide-1):** cryst. from dil. alc., m.p. 126° u.c. (110). [From $\bar{C}$ with $ClSO_3H$ as directed (110) followed by conv. of the intermediate 2-chlorotoluenesulfonyl chloride-5, cryst. from pet. ether, m.p. 63° u.c. (110), with $(NH_4)_2CO_3$.]

3:8245 (1) Matthews, *J. Am. Chem. Soc.* **48**, 570 (1926). (2) Wibaut, *Rec. trav. chim.* **32**, 247 (1913). (3) Feitler, *Z. physik. Chem* **4**, 71–72 (1889). (4) Timmermans, Hennaut-Roland, *J. chim. phys.* **27**, 410–411 (1930). (5) Perkin, *J. Chem. Soc* **69**, 1203 (1896). (6) Stuckey, Saylor, *J. Am Chem. Soc.* **62**, 2923 (1940). (7) Norris, Turner, *J. Am Chem. Soc.* **61**, 2128–2131 (1939). (8) Wahl, Normand, Vermeylen, *Bull. soc. chim.* (4) **31**, 570–583 (1922). (9) Kohlrausch, Pongratz, *Monatsh.* **63**, 441 (1934). (10) Timmermans, *Bull. soc. chim Belg.* **36**, 505 (1927).

(11) Rule, McLean, *J. Chem. Soc.* **1931**, 689. (12) Haase, *Ber.* **26**, 1053 (1893). (13) Linard, *Bull. soc. chim Belg.* **34**, 369, 393 (1925). (14) Seubert, *Ber.* **22**, 2520 (1889). (15) Chindraux, *Helv. Chim Acta* **12**, 925–927 (1929). (16) Timmermans, *Bull. soc chim. Belg.* **43**, 633–634 (1934). (17) Marvel, McElvain, *Org Synthese* [illegible]
163–165 (1932); **3**, 33–35 (1923). (18) Erdm[illegible]
Nissen, *Ann.* **269**, 393–394 (1892). (20) Helle[illegible]

(21) Heller, *Z. angew. Chem.* **23**, 389–392 [illegible]

3:8270 3-CHLOROBUTEN-2-OL-1 (2-Chlorobuten-2-ol-4; γ-chlorocrotonyl alcohol)

Cl
|
CH_3—C=CH—CH_2OH

C_4H_7OCl Beil. S.N. 25

B.P. 161–162°		(1)	D_4^{20} = 1.1139 (1)	n_D^{20} = 1.4678 (1)
92–93°	at 50 mm.	(2)	1.1128 (2)	1.4652 (3) (4)
92°	at 50 mm.	(3) (4)		1.4649 (2)
78.5–79°	at 25 mm.	(1)	D_4^{17} = 1.1172 (5)	n_D^{17} = 1.4654 (5)
67–67.5°	at 12 mm.	(5)		
56.5°	at 9 mm.	(6)	D_4^{15} = 1.1185 (1)	n_D^{15} = 1.4698 (1)

[For prepn. of C̄ from 1,3-dichlorobutene-2 (3:5550) by hydrolysis with steam (6), or *aq.* alk. (4) (6), or *aq.* K_2CO_3 (2), aq. Na_2CO_3 (70–80% yield (3)) or $CaCO_3$ (5) see indic. refs.; note that the ether corresp. to C̄ (see below) is always formed as a by-product (4) and also that *alc.* KOH does not yield C̄ but the corresponding ethers (see below); for prepn. of C̄ *from 1-bromo-3-chlorobutene-3 ("chloroprene hydrobromide")* by refluxing 2 hrs. with *aq.* Na_2CO_3 (80% yield) see (1).]

C̄ refluxed with 16% H_2SO_4 yields (2) methyl vinyl ketone.

Ethers of C̄. *Di-(3-chlorobuten-2-yl-1) ether:* from C̄ in aq. KOH by addn. of 1 mole 1,3-dichlorobutene-2 (3:5550) (80–90% yield (3)) (4); b.p. 142° at 50 mm., (3) (4) D_{20}^{20} = 1.171 (3), 1.1171 (4); n_D^{20} = 1.4860 (3) (4).

Methyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with MeOH + alk. (7), b.p. 125–126° (7).

Ethyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with excess conc. alk. EtOH (80–90% yield (3)) (4) (7): b.p. 143° (3) (4), 88–89° at 129 mm. (7), 62–64° at 40 mm. (3) (4); D_4^{20} = 0.9788 (7), D_{20}^{20} = 0.9729 (3) (4); n_D^{20} = 1.4392 (7), 1.4382 (3) (4).

Phenyl 3-chlorobuten-2-yl-1 ether: from 1,3-dichlorobutene-2 (3:5550) with alk. + phenol (7); b.p. 94° at 1 mm., D_4^{20} = 1.1080, n_D^{20} = 1.5378 (7).

Esters of C̄. *3-Chlorobuten-2-yl-1 acetate:* from C̄ with AcCl (1); b.p. 80.5–81.5° at 25 mm. D_4^{20} = 1.1029, n_D^{20} = 1.4495 (1).

C̄ readily adds Br_2 yielding (1) 2,3-dibromo-3-chlorobutanol-1, b.p. 111–112.5° at 10 mm., D_4^{20} = 2.0058, n_D^{20} = 1.5544 (1).

Ⓓ **3-Chlorobuten-2-yl-1** ***N*-(α-naphthyl)carbamate:** cryst. from lgr., m.p. 107–108° (5).

Ⓓ **3-Chlorobuten-2-yl-1 3,5-dinitrobenzoate:** m.p. 72–73° (6).

3:8270 (1) Petrov, *J. Gen. Chem. (U.S.S.R.)* **10**, 1418–1424 (1940); *C.A.* **35**, 3593 (1941). (2) Churbakov, *J. Gen. Chem. (U.S.S.R.)* **10**, 977–980 (1940); *C.A.* **35**, 2469 (1941). (3) Klebanskii, Chevuichalova, *Sintet. Kauchuk* **1935**, No. 6, 16–21; *Cent.* **1936**, I 1975; *C.A.* **30**, 1024 (1936). (4) Klebanskii, Tzyurikh, Dolgopol'skii, *Bull. acad. sci. (U.S.S.R.)* **1935**, No. 2, 189–226; *Cent.* **1935**, II 3844; *C.A.* **30**, 1259 (1936) (full English translation in *Rubber Chem. Tech.* **9**, 383–408 (1936)). (5) Tishchenko, *J. Gen. Chem. (U*
31, 5754 (1937). (6) Collins (to du Pont),
(7) Berchet (to du Pont), U.S. 2,079,758, Ma

(109) Morgan, Glover, *J. Chem. Soc.* **125**, 1597–1601 (1924). (110) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 512–513 (1940).

3:8250 1-CHLOROHEPTANE $CH_3.(CH_2)_5CH_2Cl$ $C_7H_{15}Cl$ Beil. I - 154
(*n*-Heptyl chloride) I_1-(56)
I_2-(117)

B.P.		F.P.	
159.5° (1)	at 759 mm. (10)	−69.5° (6)	D_4^{20} = 0.8766 (10)
159.2°	at 750 mm. (2)		0.8725 (6)
158.8–160.0°	(3)		n_D^{20} = 1.42844 (4)
158.5–159.5°	(4)		1.42571 (10)
117.0–117.5° cor. at 163 mm.	(5)		D_4^{15} = 0.8783 (6)
61.4°	at 27 mm. (6)		

[For prepn. of Č from heptanol-1 (1:6240) by shaking 2 days with conc. HCl + $ZnCl_2$ in cold (60% yield (4)) see (4) (8); with PCl_3 + $ZnCl_2$ (70% yield), PCl_5 + $ZnCl_2$ (78% yield), or $SOCl_2$ + pyridine (81% yield) see (4); with $SOCl_2$ but without pyridine (80% yield) see (10), with conc. HCl in s.t. at 120–130° see (2); with HCl over Al_2O_3 at 420–440° see (7); for formation from *n*-heptylamine + NOCl see (8); for formation during chlorination of *n*-heptane see (9).]

[For study of reaction of Č with KI in acetone see (5); for difficulty in forming R.MgCl see (1); note, however, that Č with Mg in dry ether + trace I_2 gives (97.5% yield (11)) RMgCl.]

Ⓓ *N*-(*n*-Heptyl)tetrachlorophthalimide: lfts from EtOH, m.p. 145–146° (12). [From Č (?) or from *n*-heptyl bromide with K tetrachlorophthalimide (12).]

3:8250 (1) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117–2120 (1934). (2) Cross, *Ann.* **189**, 3 (1877). (3) Kohlrausch, Köppl, *Monatsh* **63**, 268 (1933). (4) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929) (5) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (6) Sherrill, *J. Am. Chem. Soc.* **52**, 1985–1988 (1930). (7) Sabatier, Mailhe, *Compt. rend.* **169**, 124 (1919). (8) Ssolonina, *Cent.* **1898**, II 888. (9) Wertyporoch, *Ber.* **66**, 737–738 (1933). (10) Vogel, *J. Chem. Soc.* **1943**, 638, 640.
(11) Houben, Boedler, Fischer, *Ber.* **69**, 1766, 1777 (1936). (12) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934).

3:8264 METHYL *d,l*-α-CHLORO-*n*-VALERATE $C_6H_{11}O_2Cl$ Beil. II - 302
$CH_3.CH_2.CH_2.CH(Cl).COOCH_3$ II_1—
II_2—

B.P. 160° at 764 mm. (1)

[For prepn. of Č from α-chloro-*n*-valeronitrile with MeOH + H_2SO_4 see (1).]

3:8264 (1) Henry, *Bull. acad. roy Belg.* (3) **36**, 241–262 (1898); *Cent.* **1898**, I 194.

[For study of system: $\bar{C}$ + $SbCl_3$ see (7).]

[$\bar{C}$ with NH_3 + cat. as directed (34) (35) yields *m*-toluidine; $\bar{C}$ with aq. NaOH in pres. of Cu at 300–400° under press. yields (51) mixt. of *o*-cresol (1:1400), *m*-cresol (1:1730), and *p*-cresol (1:1410).]

[$\bar{C}$ on mononitration, e.g., with 4 pts. HNO_3 (D = 1.52) at 0°, gives a mixt. contg. (36) cf. (37) (13) (38) 59% 3-chloro-6-nitrotoluene [Beil. V-327, V_1-(162)], m.p. 24.9°, + 32% 3-chloro-4-nitrotoluene [Beil. V-329, V_1-(163)], m.p. 24.2°, + 9% 3-chloro-2-nitrotoluene [Beil. V-327, V_1-(162)], m.p. 23.4°. — $\bar{C}$ on dinitration, e.g., with mixt. of 2 wt. pts. HNO_3 (D = 1.52) + 3 wt. pts. conc. H_2SO_4 at room temp. for 12–18 hrs. (13), gives (95.8% yield (13)) 3-chloro-4,6-dinitrotoluene [Beil. V-344, V_1-(168)], cryst. from alc. or lgr., m.p. 91° (13) (38) (39), 90–90.5° (52) (note that the isomeric 3-chloro-2,6-dinitrotoluene [Beil. V_1-(168)] (40), m.p. 77° (40), and 3-chloro-2,4-dinitrotoluene, m.p. 92° (41), are also known but prepd. by indirect means). — $\bar{C}$ on trinitration, e.g., by refluxing with 3 pts HNO_3 (49.4°Bé) + 3 pts. H_2SO_4 (66°Bé) at 160° (42), yields 3-chloro-2,4,6-trinitrotoluene [Beil. V-349], cryst. from C_6H_6 + lgr., m.p. 150–151° (52), 148.5° (42).]

[$\bar{C}$ with Na followed by CO_2 as directed gives (yields: 88% (43A), 58% (43B)) *m*-toluic acid (1:0705), m.p. 110–111°, also obtd. in small yield (44) from $\bar{C}$ + alc. KCN in pres. of $NiCl_2$, htd. in s.t. at 260–270° for 20 hrs.]

[$\bar{C}$ with CrO_2Cl_2 gives a cpd. which with aq. gives (44.5% yield (45)) *m*-chlorobenzaldehyde (3:6475).]

$\bar{C}$ on oxidn. with $K_2Cr_2O_7$ + H_2SO_4 (14), with 5% aq. $KMnO_4$ (11) (46) or with dil. HNO_3 in s.t. at 130–140° for 10 hrs. (15) gives (75% yield (46)) *m*-chlorobenzoic acid (3:4392).

Ⓓ **3-Chloro-6-sulfonamidotoluene (4-chloro-2-methylbenzenesulfonamide)**: cryst. from dil. alc., m.p. 184–185° u.c. (47). [From $\bar{C}$ with $ClSO_3H$ as directed (47) followed by treatment of the resultant 4-chloro-2-methylbenzenesulfonyl chloride, cryst. from pet. eth., m.p. 52–53° u.c. (47), 54° (49) with $(NH_4)_2CO_3$.]

3:8275 (1) Feitler, *Z. physik. Chem.* **4**, 73–76 (1889). (2) Norris, Turner, *J. Am. Chem. Soc.* **61**; 2128–2131 (1939). (3) Kohlrausch, Pongratz, *Monatsh.* **63**, 441 (1934). (4) Stuckey, Saylor, *J. Am. Chem. Soc.* **62**, 2923 (1940). (5) Wibaut, *Rec. trav. chim.* **32**, 286 (1913). (6) Rule, McLean, *J. Chem. Soc* **1931**, 689. (7) Menschutkin, *J. Russ. Phys.-Chem. Soc.* **44**, 1940 (1912); *Cent.* **1913**, I 805. (8) Haase, *Ber.* **26**, 1053 (1893). (9) Seubert, *Ber.* **22**, 2520, 2522 (1889).

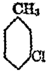
). (12) Wibaut, *Rec. trav. chim.*
(1900). (14) Wroblewski, *Ann.*
-1059 (1892). (16) Klages, *Ber.*
–3023 (1894). (18) Autenrieth,
1069 (1916). (20) Willstätter,

(21) Cohen, Dakin, *J. Chem. Soc.* **79**, 1117–1118 (1901). (22) Jenkins, *J. Am. Chem. Soc.* **55**, 2897 (1933). (23) Sampey, Fawcett, Morehead, *J. Am. Chem. Soc.* **62**, 1839–1840 (1940).
105, 1911–
au, *Compt.*
er, Albert,
Cent **1931**,
II 908.

(31) I.G., Brit 394,995, Aug. 3, 1933; *Cent.* **1933**, II 2753. (32) Houben, Fischer, *Ber.* **64**, 2649 (1931). (33) Kunckell, *Ber.* 4
May 5, 1932; *Cent.* **1932**, II 1237.
10, 1934; *Cent.* **1934**, II 1846. (36)
Chem. Soc. **38**, 1327–1333 (1916).
(1900). (39) Sane, Joshi, *J. Indian. Chem. Soc.* **5**, 300 (1928). (40) Lindemann, Pabst, *Ann.* **462**, 43 (1928).

(41) Brady, Bowman, *J. Chem. Soc.* **119**, 896–897 (1921). (42) Réverdin, Dresel, Déletra,

3:8275 *m*-CHLOROTOLUENE



C_7H_7Cl Beil. V - 291
V_1-(150)
V_2-(226)

B.P.		F.P.	
162.2°	at 756.5 mm. (1)	−48.0° (7)	D_4^{20} = 1.07218 (9)
161.8–162°	at 768 mm. (2)	(6)	n_D^{18-20} = 1.5214 (9)
161.8–161.9°	(3)	−47.8° (8)	$D_4^{18.7}$ = 1.0760 (10)
161.74–161.75°	at 760 mm. (4)		$n_D^{18.7}$ = 1.52252 (10)
161.6°	at 760 mm. (5)		$D_4^{13.9}$ = 1.0797 (10)
45.5°	at 12 mm. (6)		$n_D^{13.9}$ = 1.52535 (10)

[For prepn. of C̄ from *m*-toluidine [Beil. XII-853, XII_1-(397)] via diazotization and use of Cu_2Cl_2 reactn. (yields: 86% (46), 80% (11)) (12) (13) or CuH (35% yield (48)) see indic. refs., from 3-chloro-4-aminotoluene [Beil. XII-989, XII_1-(436)] via diazotization followed by boilg. with alc. (60% yield (14)) or conversion to corresp. hydrazine and subsequent oxidn. with $CuSO_4$ (50% yield (15)) see indic. refs.; from 5-chloro-2-aminotoluene [Beil. XII-835] with alc. H_2SO_4 + ethyl nitrite (1) or by diazotization, reduction to the corresp. hydrazine, and oxidn. of latter with $CuSO_4$ (43–63% yield (15)) see indic. refs.: for formn. of C̄ from 1-methylcyclohexanone-3 by conversion with PCl_5 to 3-chloro-1-methylcyclohexene-*x*, treatment with Br_2, and boilg. with quinoline see (16); from 3-chloro-1-methylcyclohexadiene-1,3 [Beil. V-116] by conv. to dibromide and boilg. with quinoline see (17), from *m*-cresol (1:1730) with PCl_5, or from tri-(*m*-tolyl) phosphate at 210° see (18): for study of formn. of C̄ by partial rearr. with $AlCl_3$ of *o*-chlorotoluene (3:8245) or *p*-chlorotoluene (3:8287) see (2).]

[C̄ with H_2 in pres. of $Pd/CaCO_3$ in alc./alk. soln. loses all its chlorine as HCl (19); C̄ with H_2 in pres. of Pt in AcOH loses HCl, but no quant. data are given (20).]

[C̄ with Cl_2 in pres. of Al/Hg yields (21) both 2,5-dichlorotoluene (3:6245) and 3,4-dichlorotoluene (3:6355) but no trace of any other isomers.]

[C̄ with Br_2 in CCl_4 at 60–80° in bright light (22) (23) or in CS_2 (23) or C̄ at 130° with Br_2 directly (24) gives (55% yield (22)) *m*-chlorobenzyl bromide, m.p. 15–15.5°, b.p. 103–105° at 8 mm. (22), b.p. 108–111° at 10 mm (24), D_{25}^{25} = 1.5652 (22); C̄ with Br_2 in CCl_4 in pres. of Al/Hg (25) or C̄ with Br_2 in AcOH in pres. of HNO_3 or HNO_3/H_2SO_4 (26) gives both 6-bromo-3-chlorotoluene, b.p. 120–125° at 15 mm. (26), 100–103° at 15 mm. (25) (note disagreement!), and 4-bromo-3-chlorotoluene, b.p. 90–93° at 12 mm. (26).] — [C̄ with Br_2 in pres. of Be yields (27) *x*,*y*-dibromo-3-chlorotoluene, m.p. 96.5°.]

[C̄ with $AlCl_3$ + HCl gas as directed undergoes partial rearr. (2) to both *o*-chlorotoluene (3:8245) and *p*-chlorotoluene (3:8287), for anal. of mixtures of the three isomers see (2).]

[C̄ with AcCl + $AlCl_3$ in CS_2 gives (60% yield (28)) 3-chloro-4-acetyltoluene (2-chloro-4-methylacetophenone), b.p. 260–262° at 760 mm. (28), b.p. 120–126° at 14 mm (29), accompanied (29) by some of the isomeric 3-chloro-6-acetyltoluene (4-chloro-2-methylacetophenone), b.p. 120–122° at 14 mm. (29). — C̄ with chloroacetyl chloride (3:5235) + $AlCl_3$ in CS_2 gives (70% yield (33)) 3-chloro-6-(chloroacetyl)toluene (ω,4-dichloro-2-methylacetophenone, m.p. 90° (33). — C̄ with β-chloropropionyl chloride (3:5690) + $AlCl_3$ in CS_2 gives (87% yield (50)) (30) 3-chloro-6-(β-chloropropionyl)toluene which on ring closure with conc. H_2SO_4 gives (50) (30) 5-chloro-7-methylindanone-1, m.p. 71° (50) (30). — C̄ with biphenyl-4,4′-*bis*-(carboxylic acid chloride) + $AlCl_3$ yields (31) 4,4′-*bis*-(4-chloro-2-methylbenzoyl)-biphenyl (used in prepn. of *bis*-anthraquinonyl derivs.).]

[C̄ with trichloroacetonitrile + $AlCl_3$ as directed (32) yields 4-chloro-2-methylbenzoic acid (3:4700).]

[Other reactns. involving only the OH group of $\bar{C}$ include the following: $\bar{C}$ with acetylene + BF_3 + HgO gives (38% yield (30)) ethylidene *bis*-(γ-chloro-*n*-propyl)acetal, b.p. 127–129° at 14 mm. (30); $\bar{C}$ with benzonitrile + HCl gas in ether gives (31) γ-chloro-*n*-propyl iminobenzoate hydrochloride; $\bar{C}$ with β-acetobromglucose + Ag_2CO_3 yields (32) tetra-acetyl-β-*d*-(γ-chloro-*n*-propyl)glucoside, m.p. 74° (for extension to prepn. of corresp. xyloside, galactoside, and lactoside see (32)).]

[$\bar{C}$ with solid KOH loses HCl on htg. giving (16) (7) (10) (1) 1,3-epoxypropane (trimethylene oxide) [Beil. XVII-6, $XVII_1$-(3)], b.p. 47.8° at 760 mm., $D_4^{25} = 0.8930$, $n_D^{24} = 1.3897$ (16) (for study of rate of reactn. see (33)).]

[$\bar{C}$ with NaOEt in abs. alc. reacts vigorously giving (38% yield (34)) ethyl γ-hydroxy-*n*-propyl ether (trimethylene glycol monoethyl ether) [Beil. I-476, I_1-(247)], b.p. 160–161° (34), *162.1–162.2°*, $D_4^{20} = 0.91691$, $n_D^{20} = 1.41666$ *(35)*, accompanied by some trimethylene glycol diethyl ether, b.p. 140° (34). — $\bar{C}$ with NaSH as directed gives (70–80% yield (34)) γ-hydroxy-*n*-propyl mercaptan, b.p. 85–90° at 15 mm. (Hg mercaptide = Hg ($SCH_2CH_2CH_2OH)_2$, pl. from butanol, m.p. 132–134° (36). — $\bar{C}$ with aq. Na_2S gives (36) *bis*-(γ-hydroxy-*n*-propyl) sulfide, visc. oil which could be neither distd. nor crystd. but which with phenyl isocyanate gave the corresp. *bis*-(phenylcarbamate), m.p. 146–148° (36). — $\bar{C}$ with $NaSCH_3$ in ether gives (76% yield (42)) γ-hydroxy-*n*-propyl methyl sulfide, b.p. 105–105.5° at 30 mm. (42). — $\bar{C}$ with benzyl mercaptan in alc. gives (88% yield (43)) benzyl γ-hydroxy-*n*-propyl sulfide, b.p. 185° at 19 mm. (43).]

[$\bar{C}$ in alk. medium reacts with phenols yielding corresp. subst. alcohols; e.g., $\bar{C}$ with phenol + alc. NaOEt (75% yield (37)) or $\bar{C}$ + phenol + aq. NaOH (80% yield (38) (39)) gives 3-phenoxypropanol-1, b.p. 158–160° at 25 mm., $n_D^{20} = 1.491$ (37) which with $ZnCl_2$ at 215° loses aq. and ring-closes (37) to chromane [Beil. XVII-52, $XVII_1$-(22)]; for corresp. reactn. with *o*-cresol (40), with *m*-cresol (41), *p*-cresol (41), β-naphthol (40), or resorcinol (40) see indic. refs.]

[$\bar{C}$ with prim. or sec. amines splits out HCl yielding corresp. subst. aminoalcohols: e.g., for reactn. of $\bar{C}$ with aniline + anhydrous Na_2CO_3 giving (67.5% yield) 3-(*N*-phenylamino)propanol-1 (*N*-(γ-hydroxy-*n*-propyl)aniline), b.p. [illegible] at 30 mm., $D_{26}^{26} = 1.063$,

for $\bar{C}$ with *ac*-

sec. amines see

(47) (55); for $\bar{C}$ with morpholine giving (75% yield) 3-(morpholino)propanol-1, b.p. 147–149° at 21 mm., $n_D^{25} = 1.4743$, $n_D^{20} = 1.4762$, see (76); for $\bar{C}$ with piperidine see (48) (56).] — [$\bar{C}$ with *ter*-amines yields corresp. quat. ammon. salts: e.g., $\bar{C}$ with $(CH_3)_3N$ in C_6H_6 in s.t. at 100° for 8 hrs. gives (92% yield (49)) γ-homocholine chloride, m.p. 173° (49); $\bar{C}$ with pyridine gives (85% yield (50)) γ-hydroxy-*n*-propyl pyridinium chloride, oil.] — [For reactn. of $\bar{C}$ with arsanilic acid (*p*-aminobenzenearsonic acid) (51), with *p*-hydroxybenzenearsonic acid (52), with ethyl β-methylaminopropionate (53), or with various carbazole derivs. (54) see indic. refs.]

[$\bar{C}$ with 1 mole thiourea htd. at 120–125° yields (57) *S*-(γ-hydroxy-*n*-propyl)isothiourea hydrochloride, cryst. from butanol, m.p. 130° (57); $\bar{C}$ with dry sodium *p*-toluenesulfonamide htd. at 160–170° for 18 hrs. yields (58) *N*-(γ-hydroxy-*n*-propyl)-*p*-toluenesulfonamide as an oil.]

[For study of rate of reactn. of $\bar{C}$ with KI in acetone at 35° and 45° see (39); for reactn. of $\bar{C}$ with Na_3AsO_3 see (5).]

—— γ-Chloro-*n*-propyl acetate [Beil. II_1-(48), II_2-(139)]: liq., b.p. 168–169° (59), 165–166° (60), 88–90° at 22 mm. (61), 66° at 14 mm. (17), 62–63° at 10 mm. (7) $D_{21}^{21} = 1.1105$ (7); $n_D^{21} = 1.431$ (7). [From $\bar{C}$ + AcCl (yields: 90% (60), 87% (16)) (7) (62), from 1,3-dichloropropane (3:5450) with AgOAc (53% yield (61)), or from

Ber. **37**, 2091–2095 (1904); *Bull. soc. chim.* (3) **31**, 633 (1904). (43A) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 754–755 (1936). (43B) Morton, Stevens, *J. Am. Chem. Soc.* **53**, 4031–4032 (1931). (44) Siebodzinski, *J. prakt. Chem.* (2) **143**, 119 (1935). (45) Law, Perkin, *J. Chem. Soc.* **93**, 1636 (1908). (46) Koopal, *Rec. trav. chim.* **34**, 144 (1915). (47) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 512–513 (1940). (48) Neogi, Mitra, *J. Chem. Soc.* **1928**, 1332. (49) I.G., Brit. 281,290, Nov. 22, 1927; French 644,319, Oct. 5, 1928; *Cent.* **1929**, *II* 352. (50) Mayer, Müller, *Ber.* **60**, 2281–2283 (1927).

(51) Britton (to Dow Chem. Co.), U.S. 1,996,744, April 9, 1935; *Cent.* **1935**, II 1962. (52) Qvist, Moilanen, *Acta Acad. Aboensis, Math. et Phys.* **14**, No. 3, 9 pp. (1943); *Cent.* **1943**, II 1268–1269; *C.A.* **38**, 5491 (1944).

3:8285 3-CHLOROPROPANOL-1 (Trimethylene chlorohydrin, γ-chloro-*n*-propyl alcohol) $CH_2.CH_2.CH_2OH$ (with Cl on the first CH_2) C_3H_7OCl Beil. I - 356, I_1-(180), I_2-(370)

B.P.				D_4^{20}		n_D^{20}	
160–162° cor.			(1) (10)	D_4^{20} = 1.1318	(9)	n_D^{20} = 1.44693	(2)
160.0–160.3°	at	734.1 mm.	(2)	1.1309	(2)	1.4469	(9)
158.6–161.0°	at	734 mm.	(3)	1.1262	(7)	1.448	(7)
158–159°			(4)				
74–76°	at	23 mm.	(5)	D_4^{18} = 1.129	(10)		
66.0–66.2°	at	16 mm.	(6)				
63–64°	at	16 mm.	(7)				
64–66°	at	14 mm.	(77)				
60–64°	at	10 mm.	(8)				
53°	at	6 mm.	(2)				

Colorless oil with agreeable odor; undergoes partial decompn. on distn. at ord. press. — Very sol. aq. but not miscible with it.

[For prepn. of Č from propanediol-1,3 (trimethylene glycol) (1.6490) with HCl gas (50–60% yield (8)) (4) (7) (11) (12) (13) (1), with conc. HCl (yield: 34% (14), 28% (15), 15% (16)) (some 1,3-dichloropropane and other prods. are also formed), with $SOCl_2$ (50–60% yield (77)), or with S_2Cl_2 (yields: 68% (5), 60% (16)) (17) see indic. refs ; for formn. of Č from γ-chloro-*n*-propyl acetate (see below) by alcoholysis with MeOH/HCl (85% yield (18)) or from γ-chloro-*n*-propyl trichloroacetate (9) by hydrol. with aq. KOH at 35° (9) see indic. refs.; for manuf. from ethylene + formaldehyde + HCl + $ZnCl_2$ see (19).]

Č on oxidn. with conc. HNO_3 gives (yields: 78–79% (20), 54–56% (21), 30–40% (13)) β-chloropropionic acid (3.0460) (note that the presumably intermediate β-chloropropionaldehyde (3:5576) is best obtd. by other means).

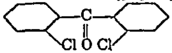
[Č with HBr gas (22), on distn. with 48% HBr (yield: 75–85% (22), 40% (11)), with HBr + H_2SO_4 (yield: 89% (23)), or with PBr_3 (94% yield (11)) gives 1-bromo-3-chloropropane (trimethylene chlorobromide) [Beil. I-109, I_1-(36), I_2-(75)], b.p. 142–145°, D_{25}^{25} = 1.4718 (24), n_D^{23} = 1.4732 (24); for study of rate of reactn. of Č with HBr in phenol see (25).]

[Č refluxed with ½ wt. conc. H_2SO_4 gives (10–15% yield (26)) *bis*-(γ-chloro-*n*-propyl) ether, b.p. 215° at 745 mm., D_{20}^{20} = 1.140 (26) — Č with SO_2Cl_2 gives (68% yield (27)) γ-chloro-*n*-propyl chlorosulfonate, b.p. 85° at 4 mm., D_0^{22} = 1.456 (27). — Č with $SOCl_2$ gives (70% yield (27)) *sym.-bis*-(γ-chloro-*n*-propyl) sulfite, b.p. 161–162° at 13 mm., D_0^{19} = 1.313 (27).]

[Č with $COCl_2$ (3:5000) directly (28) or in toluene (29) gives (43% yield (29)) γ-chloro-*n*-propyl chloroformate (3:6895); Č with trichloroacetic acid (3.1150) gives (57% yield (9)) γ-chloro-*n*-propyl trichloroacetate, b.p. 107° at 8 mm., D_4^{15} = 1.4732, n_D^{15} = 1.4830 (9); *for formn. of other esters (as derivs.) see below.*]

berg, Bailar, *J. Am. Chem. Soc.* **51**, 2231 (1929). (17) Meisenheimer, Meis, *Ber.* **57**, 295 (1924). (18) Cathcart, Meyer, *Ber.* **25**, 1498, 3295 (1892). (19) Montagne, *Rec. trav. chim.* **26**, 266 (1907). (20) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; *C.A.* **39**, 4097 (1945).

3:0717 2,2'-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. S.N. 652
(Di-(*o*-chlorophenyl) ketone)



M.P. 45.4–46.6° cor. (1) B.P. 127–135° at 1 mm. (1)
45–46° (1)

[For prepn. of Č from 2,2'-dichlorobenzilic acid (1) by oxidn. with CrO_3/AcOH (47% yield (1)) or from di-(*o*-chlorophenyl)carbinol (1) by oxidn. with $Na_2Cr_2O_7/H_2SO_4$/AcOH see indic. refs.]

Ⓓ 2,2'-Dichlorobenzophenone 2,4-dinitrophenylhydrazone: m.p. 206–208° (1).

3:0717 (1) Haller, Bartlett, Drake, Newman, Cristol et al., *J. Am. Chem. Soc.* **67**, 1600–1601 (1945).

3:0720 ETHYLENE GLYCOL *bis*-CHLOROACETATE $C_6H_8O_4Cl_2$ Beil. S.N. 160

$ClCH_2.CO.O.CH_2$
$ClCH_2.CO.O.CH_2$

M.P. 45–46.5° (1) B.P. 142–144° at 2 mm. (1)

Cryst. from ether/pet. eth. — Insol. aq. (dif. from β-hydroxyethyl chloroacetate (3:6780)).

[For prepn. of Č from ethylene oxide (1:6105) with chloroacetic acid (3:1370) as by-product of prepn. of β-hydroxyethyl chloroacetate (3:6780) see (1); note also that Č is formed (together with ethylene glycol (1:6465)) by disproportionation of β-hydroxyethyl chloroacetate (3:6780) on long stdg. in ord. glass bottles (1).]

Č on shaking with aq. is hydrolyzed only very slowly (1).

[For use of Č as insecticide, fungicide, and disinfectant see (2).]

3:0720 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 316–318 (1933). (2) Peet (to Rohm and Haas Co.), U.S. 1,816,441, July 28, 1931; *Cent.* **1932**, I 1146; *C.A.* **25**, 5501 (1931); French 667,633, Oct. 18, 1929; *Cent.* **1930**, I 2614.

trimethylene glycol (1:6490) with Ac_2O + S_2Cl_2 (68% yield (17)).] — [This acetate with solid KOH loses HOAc giving (16) (7) (61) 2,3-epoxypropane (trimethylene oxide) (see above).]

—— γ-*Chloro-n-propyl benzoate*: oil, b.p. 154–156° at 22 mm. (31), 155–156° at 15 mm. (4), 133–134° at 2 mm. (39), D_4^{22} = 1.1672 (31), n_D^{20} = 1.5136 (31). [From C̄ + BzCl (yields: 84% (39), 75% (4)) or from γ-chloro-n-propyl iminobenzoate hydrochloride (see above) by hydrol. (31).] — [For reactn. of this ester with pyrrolidine (63), pyrroline (63), piperidine (56), subst. piperidines (64) (65) (68), hydrogenated quinolines (66), or with *N*-methyl-phenyl-alkylamines (67) see indic. refs.]

—— γ-*Chloro-n-propyl p-nitrobenzoate*: oil, b.p. 168.5–169.5° at 2 mm., D_{25}^{25} = 1.3222, n_D^{25} = 1.54736 (67). [From C̄ + *p*-nitrobenzoyl chloride on htg. (67).]

Ⓓ γ-Chloro-n-propyl 3,5-dinitrobenzoate: colorless pl. from lt. pet., m.p. 77° (17). [From C̄ + 3,5-dinitrobenzoyl chloride (17).]

—— γ-Chloro-n-propyl hydrogen phthalate: unreported.

—— γ-Chloro-n-propyl hydrogen 3-nitrophthalate: unreported.

—— γ-*Chloro-n-propyl benzenesulfonate*: unreported.

—— γ-Chloro-n-propyl *p*-toluenesulfonate: oil, b.p. 216–219° at 17 mm. (69), 188–192° at 5 mm (24), D_4^{20} = 1.2674 (69), D_{25}^{25} = 1.2396 (24), n_D^{20} = 1.5230 (69), n_D^{21} = 1.5225 (24). [From C̄ + *p*-toluenesulfonyl chloride on htg. (69) or with aq. NaOH at 15° (50–55% yield (24)).] — [For reactn. of this ester with RMgX cpds. see (69) (24), with various sodium acetylenes see (70).]

—— γ-*Chloro-n-propyl carbamate*: *pearly cryst. from hot. aq., m.p. 62° (29).* [From C̄ with urea nitrate (2 moles) on htg. at 130–135° (16% yield (29)) or from γ-chloro-n-propyl chloroformate (3:6010) with conc. aq. NH_4OH (29).]

—— γ-Chloro-n-propyl *N*-(phenyl)carbamate: ndls. from alc., m.p. 38° (29), m.p. 35–36° (28), b.p. 190° at 3.5 mm. (28). [From C̄ + phenyl isocyanate at 150° (29) or from γ-chloro-n-propyl chloroformate (3:6010) with aniline (29).]

—— γ-*Chloro-n-propyl N-(p-nitrophenyl)carbamate*: *unreported.*

Ⓓ γ-Chloro-n-propyl *N*-(α-naphthyl)carbamate, cryst. from hot lgr., m.p. 76° (71) (17), 76.5° (9), 75.5–76.5° (28). [From C̄ + α-naphthyl isocyanate (71).]

Ⓓ *N*-(γ-Hydroxy-n-propyl)phthalimide [3-(*N*-phthalimido)propanol-1] [Beil. XXI-472]: cryst. from aq., m.p. 75° (72), 74° (73), 88° (74). [From C̄ + K phthalimide at 190° (73); also indirectly as cited in other indicated refs.]

Ⓓ *N*-(γ-Hydroxy-n-propyl)tetrachlorophthalimide [3-(*N*-tetrachlorophthalimido)propanol-1)]: pr. from acetone, m.p. 165–166° (75). [From C̄ with K tetrachlorophthalimide as directed (75).]

3:8285 (1) Reboul, *Ann. chim.* (5) **14**, 493–496 (1878). (2) Karvonen, *Ann. Acad. Sci. Fennicae* **A-3**, No. 7, 1–103, *Cent.* **1912**, II 1271, *C.A.* **14**, 2175–2176 (1920); *Ann. Acad. Sci. Fennicae* **A-5**, No. 6, 120. (3) Kohlrausch, Ypsilanti, *Z. physik. Chem.* **B-32**, 414 (1936). (4) Zaki, *J. Chem. Soc.* **1930**, 2271. (5) Gough, King, *J. Chem. Soc.* **1928**, 2439. (6) Smyth, Walls, *J. Am. Chem. Soc* **54**, 2263 (1932). (7) Lespieau, *Bull soc. chim.* (5) **7**, 254–255 (1940). (8) Marvel, Calvery, *Org Syntheses*, Coll. Vol. 1 (2nd ed), 533–535 (1941); (1st ed), 519–521 (1932); **8**, 112–115 (1928). (9) Gayler, Waddle, *J. Am. Chem. Soc.* **63**, 3358–3359 (1941). (10) Ipatov, *J. Russ Phys.-Chem. Soc.* **46**, 64 (1914); *Cent.* **1914**, I 2161.

(11) Cloke, Anderson, Lachmann, Smith, *J. Am. Chem. Soc.* **53**, 2793–2794 (1931). (12) Smith, Wode, Widhe, *Z. physik. Chem.* **130**, 164 (1927). (13) Rojahn, *Ber.* **54**, 3116–3117 (1921). (14) Hultman, Davis, Clarke, *J. Am. Chem. Soc* **43**, 369–370 (1921). (15) Norris, Mulliken, *J. Am. Chem Soc.* **42**, 2095–2096 (1920). (16) Derick, Bissell, *J. Am Chem. Soc.* **38**, 2481–2486 (1916). (17) Bennett, Heathcoat, *J. Chem. Soc.* **1929**, 269–271. (18) Henry, *Bull. acad. roy. Belg* **1906**, 732–740 (1907); *Cent.* **1907**, I 1314. (19) I.G., Brit. 465,467, June 3, 1937; French 812,292, May 4, 1937; *Cent.* **1937**, II 1445. (20) Powell, Huntress, Hershberg, *Org Syntheses*, Coll. Vol. 1 (2nd ed.), 168–169 (1941).

(21) Powell, *Org Syntheses*, Coll. Vol. 1 (1st. ed.), 162–163 (1932); **8**, 58–59 (1928); *J. Am. Chem.*

Soc. **46**, 2879 (1924). (22) Allen, *Org. Syntheses*, Coll. Vol. **2** (2nd ed.), 157, Note 2 (1941); Coll. Vol. **1** (1st ed.), 150– [illegible]
Soc. **42**, 307 (1920). [illegible]
Bennett, Reynolds, [illegible]
2228–2229 (1921). [illegible]
Chem. Soc. **45**, 791–7 [illegible]
land, Vogt, Foohey, [illegible]

(31) Cloke, Keniston, *J. Am. Chem. Soc.* **60**, 129–130 (1938). (32) Coles, Dodds, Bergeim, *J. Am. Chem. Soc.* **60**, 1021–1022 (1938). (33) Petrenko-Kritschenko, Konschin, *Ann.* **342**, 56 (1905). (34) Rojahn, Lemme, *Arch. Pharm.* **263**, 617, 619 (1925). (35) Karvonen, *Ann. Acad. Sci. Fennicae* **A-10**, No. 9, p. 7. (36) Bennett, Hock, *J. Chem. Soc.* **127**, 2673 (1925). (37) Rindfusz, *J. Am. Chem. Soc.* **41**, 668–669 (1919). (38) Powell, *J. Am. Chem. Soc.* **45**, 2709–2710 (1923). (39) Kirner, *J. Am. Chem. Soc.* **48**, 2745–2751 (1926). (40) Rindfusz, Ginnings, Harnack, *J. Am. Chem. Soc.* **42**, 160–165 (1920).

(41) Powell, Johnson, *J. Am. Chem. Soc.* **46**, 2862–2863 (1924). (42) Kirner, *J. Am. Chem. Soc.* **50**, 2452 (1928). (43) Rothstein, *J. Chem. Soc.* **1934**, 686. (44) Rindfusz, Harnack, *J. Am. Chem. Soc.* **42**, 1723 (1920). (45) Davis, Brewster, Blair, Thompson, *J. Am. Chem. Soc.* **44**, 2640–2641 (1922). (46) Coles, Lott, *J. Am. Chem. Soc.* **58**, 1989 (1936). (47) Burnett, Jenkins, Peet, Dreger, Adams, *J. Am. Chem. Soc.* **59**, 2249–2250 (1937). (48) Brill, *J. Am. Chem. Soc.* **47** [illegible] –247 (1932). (50) Barnes, Adams, *J* [illegible] veet, Hamilton, *J. Am. Chem. Soc.* **5**[illegible] (1924). (54) Burtner, Lehmann, *J* [illegible] ll, B. K. Campbell, *Proc. Indiana Acad. Sci.* **49**, 101–104 (1939); *C.A.* **35**, 5460 (1941). (56) McElvain, *J. Am. Chem. Soc.* **49**, 2838 (1927). (57) Olin, Davis, *J. Am. Chem. Soc.* **52**, 3323 (1930). (58) Peacock, Givan, *J. Chem. Soc.* **1937**, 1470. (59) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* **47**, 498–499 (1925). (60) Bogert, Slocum, *J. Am. Chem. Soc.* **46**, 766 (1924).

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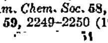
(71) Bickel, French, *J. Am. Chem. Soc.* **48**, 747–749 (1926). (72) Gabriel, *Ber.* **38**, 633 (1905). (73) Gardner, Haenni, *J. Am. Chem. Soc.* **53**, 2766–2767 (1931). (74) Garelli, Racciu, *Atti accad. sci. Torino, Classe sci. fis. mat. nat.* **69**, 358–363 (1934); *Cent.* **1934**, II 2823. (75) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934). (76) Cheney, Bywater, *J. Am. Chem. Soc.* **64**, 970 (1942). (77) Rovira, Halasz, *Compt. rend.* **212**, 644 (1941).

3:8287 *p*-CHLOROTOLUENE



C_7H_7Cl Beil. V - 292; V_1-(150); V_2-(226)

B.P.		M.P.		
163.5° cor. at 764 mm.	(1)	+7.8°	(8)	D_4^{25} = 1.065 (16)
162.4° at 760 mm.	(2)	7.5°	(14) (15) (16)	n_D^{25} = 1.51895 (9)
	(3)			$D_4^{24.35}$ = 1.0651 (21)
162.3° at 756.4 mm.	(4)	7.4°	(17) (4)	$n_D^{24.35}$ = 1.51925 (21)
162.0–162.2° cor.	(5)	7.15–7.30°	(7)	D_4^{20} = 1.0700 (9)
162–163°	(6)	7.1°	(18)	1.06974 (17)
161.98–161.99° at 760 mm.	(7)	7°	(6) (19)	1.069 (21)
161.7–162.2° cor. at 759.9 mm.	(8)	6.86°	(12)	n_D^{20} = 1.521 (21)
161.5–161.9° at 760 mm.	(9)	6.85°	(20)	See also
161.0–161.4°	(10)			Note 3.
160.6–161.2°	(11)	See also Note 2.		n_D^{19} = 1.5223 (22)
162.1° u.c. at 755 mm.	(12)			

55.57°	at	16 mm.	(3)
54.28°	at	15 mm.	(3)
52.86°	at	14 mm.	(3)
48°	at	12 mm.	(13)
45.5°	at	12 mm.	(14)
44°	at	10 mm.	(15)

$n_D^{15} = 1.5221$ (12)

See also Note 4.

See also Note 1.

Note 1. For further data on b.p. of $\bar{C}$ at 16 pressures from 74–764 mm. see (4).

Note 2. For effect of press on m.p see (20).

Note 3. For data on D_4^t from $t = 25°$ to $t = 160°$ see (16) (4); note also $D_{20}^{20} = 1.0714$ (8).

Note 4. For n_D^{19}/compn. data on system: $\bar{C}$ + o-chlorotoluene (3:8245) see (22).

$\bar{C}$ with aq. forms a const.-boilg mixt., b.p. 95° (use in sepn. of $\bar{C}$ from polychlorotoluenes (23)). — For f p./compn. data on system: $\bar{C}$ + o-chlorotoluene (3:8245) (eutectic, f.p. −49 8°, contg. 27 wt % $\bar{C}$) see (8) (147); for D_{20}^{20}/compn. data (8) and for n_D^{19}/compn. data (22) on this system see indic. refs. — For f p /compn. data on systems of $\bar{C}$ with *p-bromotoluene* or with *p-fluorotoluene* see (19). — For data on const.-boilg. mixts. of $\bar{C}$ with various org cpds see Beil. V_2-(227). — For cryoscopic constant (i e., lowering of f.p. per mole solute per 1000 g $\bar{C}$) viz , 5 53 (12), 5 6 (24), 5 97 (25), see indic. refs.; for use in detn of $\bar{C}$ in mixt. with o-chlorotoluene (3:8245) and m-chlorotoluene (3:8275) see (25).

[For prepn. of $\bar{C}$ from p-toluidine via diazotization in HCl and warming the resultant solution as such (yields: 60% (26), 40–44% (27)) (28) or in pres. of Cu_2Cl_2 (yields: 95% (33), 88–89% (29), 81% (31), 70–79% (30), 63.5% (32)) [for study of kinetics of this reaction see (34) (35)], or in pres of Cu powder (63.8% yield (36)), or in pres. of CuH (64% yield (37)), or by electrolysis between Cu electrodes in pres. of $CuCl_2$ (38) see indic. refs.; for prepn. of $\bar{C}$ from p-toluidine via diazotization, conversion to solid p-toluenediazonium chloride, and subsequent warming with C_6H_6 + $AlCl_3$ (39), or via diazotization, conversion of diazonium salt to its cpd. with $PbCl_4$, and subsequent htg. of latter in naphthalene at 150° (40), see indic. refs.]

[For formn. of $\bar{C}$ (usually together with other prods) from toluene (1:7405) with Cl_2 (70) in pres. of Fe in diffuse light in cold (8) (gives mixt. contg. 42% $\bar{C}$ + 58% o-chlorotoluene (3:8245) (8) (22)), or in pres. of I_2 (22) (41) (42), or in pres. of $PbCl_2$ (8), $SbCl_5$ (41), $MoCl_5$ (43) (28) (44), or Al/Hg (45); for formn of $\bar{C}$ from toluene by electrolysis in strong HCl (46) or in AcOH/conc. HCl in dark (47) see indic. refs.; for formn. of $\bar{C}$ from toluene with SO_2Cl_2 at 160° (48), with SO_2Cl_2 in pres. of various cat. in dark (49), with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 at 70° (50), with pyrosulfuryl chloride + $AlCl_3$ at 0° (51), with HCl + HNO_3 at 100° (52), with n-butyl chlorosulfonate + $AlCl_3$ (6 2% yield (53)), with anhydrous $FeCl_3$ after refluxing 1½ hrs. (65% yield (54)), or with NCl_3 (55) see indic. refs.]

[For formn. of $\bar{C}$ from o-chlorotoluene (3:8245) or m-chlorotoluene (3:8275) by partial rearr. with $AlCl_3$ + HCl gas see (25); from tetra-(p-tolyl)tin with Cl_2 in $CHCl_3$ (85% yield (6)) or from tri-(p-tolyl) stibine dichloride on htg. under 5–7 mm. press. at 60–65° (56) (note that at 160–200° di-p-tolylstibine chloride is formed (56)) or from tri-(p-tolyl)-phosphite dichloride by htg at 200–210° (57) see indic. refs.; from p-tolyl MgBr in ether with Cl_2 (58) or with benzenesulfonyl chloride (59) see indic. refs.; from p-toluenediazopiperidide with conc. HCl see (60); from p-chlorobenzaldehyde (3:0765) on elec. reduction in acid soln. with Cu cathode see (61); from chlorobenzene (3:7903) via condensation with CH_2O + HCl to p-chlorobenzyl chloride (3:0220) and subsequent reductn. with Zn + NaOH see (62)]

[C̄ on pyrolysis over red-hot Pt yields (63) mainly 4,4′-dichlorodibenzyl (1,2-*bis*-(*p*-chlorophenyl)ethane [Beil. V-600, V_1-(281), V_2-(507)], colorless lfts. from alc., m.p. 112°, accompanied by a very small amt. 4,4′-dichlorostilbene (1,2-*bis*-(*p*-chlorophenyl)ethylene) [Beil. V_1-(304), V_2-(539)], ndls. from alc., m.p. 170°.]

[C̄ with H_2 in pres. of $Pd/CaCO_3$ (64) or reduced Ni (65) in alc./alk. soln. loses all its halogen as HCl; C̄ with Na in liq. NH_3 as directed (66) yields toluene and other prods.; C̄ with HI + P in s.t. at 302° for 5 hrs. gives (80% yield (67)) toluene.]

C̄ on oxidn. with 3 pts. $KMnO_4$ in dil. aq. soln. under reflux for 4–5 hrs. (68) (51), or with CrO_3 (42), or with dil. HNO_3, e g., with 6 pts. of dil. HNO_3 (1 vol. conc. HNO_3 + 2 vols. aq.) at 145° for 1½ hrs. (69) or at 115–120° for 5–6 hrs. (70), yields *p*-chlorobenzoic acid (3:4940), m.p. 243° (for use in quant. estn. of C̄ in pres. of toluene, benzyl chloride, and *o*-chlorotoluene see (70)). — Note that with HNO_3 C̄ is more rapidly oxidized than *o*-chlorotoluene, *m*-chlorotoluene, or the various dichlorotoluenes but more slowly than *p*-bromotoluene (69). — C̄ on oxidn. with air at 260° in pres. of Na_2CO_3 and under press. (71), or on vapor-phase oxidn. over suitable cat. (72), or on electrolytic oxidn. in dil. Na_2CO_3 soln. at 60° (73) cf. (74), or even on very long stdg. (2 years) with I_2 + aq. in sunlight (75) gives *p*-chlorobenzoic acid. — C̄ with N_2O_4 yields (76) *p*-chlorobenzoic acid accompanied by nitration prods.

[C̄ with chromyl chloride (CrO_2Cl_2) yields an addn. prod. which with aq. gives in good yield (77) *p*-chlorobenzaldehyde (3:0765). — C̄ with air in aq. susp. of FeO.OH + cat. at 235–240° and 50–60 atm. press. gives (78) a mixt. of *p*-chlorobenzaldehyde (3:0765) + *p*-chlorobenzoic acid (3:4940).]

[C̄ with Cl_2 or on htg. with $PbCl_4.2NH_4Cl$ or with SO_2Cl_2 in pres. of dibenzoyl peroxide in dark yields *p*-chlorobenzyl chloride (3:0220), q.v. for relevant refs. — C̄ with 2 moles Cl_2 in pres. of 5% PCl_5 at 160–170° gives (79) (80) *p*-chlorobenzal (di)chloride (3:6700). — C̄ with 3 moles Cl_2 at high temp. in u.v. light (81) cf. (82) or with 3 moles Cl_2 (83) in pres. of $FeCl_3$ (84) or of PCl_5 (85) (86) gives (93% yield (85)) *p*-chlorobenzotrichloride (3:6825) q.v. — C̄ with Cl_2 (1 mole) in pres. of 1% Fe or 40% $PbCl_2$ at 20° gives (65% yield (87)) a mixt. comprising 58.4% 2,4-dichlorotoluene (3:6290) + 41.6% 3,4-dichlorotoluene (3:6355).]

[C̄ with Br_2 at 130° (88) or at 160° (89) (90) or in pres. of dibenzoyl peroxide in dark at 100° (91) gives (21% yield (90)) exclusively (91) *p*-chlorobenzyl bromide [Beil. V-307, V_2-(239)], cryst. from MeOH, m.p. 62–63° (88), ndls. from 85% alc., m.p. 50° (90), 51° (79), 48.5° (89); for study of rate of side-chain bromination of C̄ in CS_2 at 57° see (92). — C̄ with 2 moles Br_2 in pres. of $BeBr_2$ (93) or in AcOH + fumg. HNO_3 + fumg. H_2SO_4 (94) gives *p*-chlorobenzal (di)bromide, m.p. 99° (93).]

[C̄ with $AlCl_3$ + HCl gas as directed (25) undergoes partial rearr. to both *o*-chlorotoluene (3:8245) and *m*-chlorotoluene (3:8275); for anal. of mixts. of the three isomers see (25).]

[C̄ with AcCl (95) or better Ac_2O (96) (97) + $AlCl_3$ in CS_2 (98) gives (yields: 85% in 4 hrs. (97), 65% (98), 34% in 2 hrs. (96)) 2-chloro-5-methylacetophenone [Beil. VII-307], b.p. 245.8–246.0° at 760.1 mm. (96), n_D^{25} = 1.5419 (96). — C̄ with β-chloropropionyl chloride (3:5690) + $AlCl_3$ in CS_2 gives (87% yield (99)) (100) 4-chloro-3-(β-chloropropionyl)toluene, oil, which on ring closure with conc. H_2SO_4 gives (72% yield (99)) (100) 7-chloro-4-methylindanone-1, cryst. from MeOH, m.p. 128° (99) (100). — C̄ with trichloroacetonitrile + $AlCl_3$ (4 moles) at 80–90° satd. with HCl gas for 2 days gives only 5% yield (101) of a mixt. of 2-chloro-5-methyl- and 5-chloro-2-methyl-ω,ω,ω-trichloroacetophenones.]

[C̄ with oxalyl (di)chloride (3:5060) + $AlCl_3$ in CS_2 for 20 hrs. at room temp. gives (40% yield (102)) 2-chloro-5-methylbenzoic acid (6-chloro-3-methylbenzoic acid) (3:4615), cryst. from aq., m.p. 163–166° (102), accompanied by some dichlorodimethyl-benzophenone, m.p. 70°, whose structure was not detd. — C̄ with fumaryl (di)chloride (3:5875) + $AlCl_3$

in CS_2 at 50–60° for 2 hrs. gives (25% yield (103)) *bis*-1,2-(2-chloro-5-methylbenzoyl)-ethylene, pale yel. cryst. from alc., m.p. 158° (103).]

[$\bar{C}$ with benzoyl chloride + $AlCl_3$ in CS_2 gives (50% yield (98)) (104) (105) 2-chloro-5-methylbenzophenone (6-chloro-3-methylbenzophenone) [Beil. VII_1-(235)], cryst. from AcOH, m.p. 35–36° (98) (104) (105), together with 5-chloro-2-methyl-(3-chloro-6-methyl)-benzophenone [Beil. VII_1-(235)], oil, b.p. 210° at 30 mm. (106). — $\bar{C}$ with *o*-chlorobenzoyl chloride (3:6640) + $AlCl_3$ in CS_2 gives (106) 5,2′-dichloro-2-methylbenzophenone [Beil. VII_1-(235)], oil, b.p. 225° at 12 mm. (106).]

[$\bar{C}$ with phthalic anhydride (1:0725) + $AlCl_3$ gives (62.5% yield on the phthalic anhydride (107)) *o*-(2-chloro-5-methylbenzoyl)benzoic acid, ndls. from C_6H_6, m.p. *164–165°* *(107)*, 165° (108), which with conc. H_2SO_4 at 75° for 4 hrs. (108) or with 8 pts. fumg. H_2SO_4 (20% SO_3) (107) ring-closes to give (yields: 93% (107), 85% (108)) 1-chloro-4-methyl-anthraquinone [Beil. VII-809, VII_1-(421)], yel. ndls. from AcOH or alc., m.p. 164° (107) (108). — Note that the structure of the above keto acid, m.p. 164–165°, has been definitely established (109) as shown and that it is *not* the isomeric *o*-(5-chloro-2-methylbenzoyl)-benzoic acid, which appears to be still unreported. — For reactn. of $\bar{C}$ with 3,6-dichloro-phthalic anhydride (3:4860) (110) or with pyromellitic anhydride (111) in pres. of $AlCl_3$ see indic. refs.]

[$\bar{C}$ does *not* (112) react with *bis*-(chloromethyl) ether (3:5245), but $\bar{C}$ with formalin + conc. HCl yields (62) 4-chloro-3-(chloromethyl)toluene since on reductn. with Zn + NaOH the prod. gives 4-chloro-1,3-dimethylbenzene (3:8665). — $\bar{C}$ with aq. vapor + CO over suitable cat. at 300–400° yields (113) *p*-toluic acid (1:0795). — $\bar{C}$ with NH_3 + CO over suitable cat. as directed (114) yields *p*-toluidine (see also below). — $\bar{C}$ with S_2Cl_2 + $AlCl_3$ in CS_2 gives (115) 4,5-dichloro-1,8-dimethylthianthrene, m.p. 195–197° (115).]

[$\bar{C}$ with Li in ether gives (63% yield (116)) *p*-tolyllithium; $\bar{C}$ with Li at 150° followed by treatment with aq. gives (117) toluene + 4,4′-dimethylbiphenyl. — $\bar{C}$ with Na in C_6H_6 treated with CO_2 at ord. temp. (118) (119) or at 50° and 500 lbs. press. (120) cf. (121) gives (yields: 95% (120), 76% (121)) *p*-toluic acid (1:0795), m.p. 178°. — $\bar{C}$ with Na treated with benzophenone as directed (122) yields diphenyl-*p*-tolyl-carbinol [Beil. VI-722, VI_1-(355)], m.p. 72–73°.]

[$\bar{C}$ on hydrolysis with aq. vapor over silica gel contg. 3% finely divided Ni at 380° (123), or with aq. vapor over cat. at 480° (124), or with aq. Na_2CO_3 in pres. of Cu at 300° under press. (125), or with 15–20% aq. NaOH at 300° (126) gives (80% yield (123)) *p*-cresol (1:1410). Note, however, claim (127) that $\bar{C}$ when hydrolyzed with 15% aq. NaOH in pres. of Cu for 2 hrs. at 315–320° yields prod. contg. not only *p*-cresol (1:1410) but also *m*-cresol (1:1730) (for extensive study of hydrolysis of $\bar{C}$ as means of prepn. of *m*-cresol see (147)). — $\bar{C}$ with H_2S at 700° over suitable cat. yields (128) thio-*p*-cresol (*p*-tolyl-mercaptan).]

[$\bar{C}$ with aq. NH_4OH + CuO at 150–250° under press. (129) or $\bar{C}$ + aq. NH_4OH + Cu salts + various anti acids at 225–230° under press. (130) (131) yields *p*-toluidine and/or di-*p*-tolylamine. — $\bar{C}$ with KNH_2 in liq. NH_3 (132) or Na in liq. NH_3 (66) yields *p* toluidine. — Note that $\bar{C}$ does not react with aq. sodium sulfanilate + Na_2CO_3 (dif. from benzyl chloride (3:8535) and use in sepn. of $\bar{C}$ from latter (8)).]

[$\bar{C}$ on mononitration yields a mixt. contg. both *4-chloro-2-nitrotoluene* [Beil. V-327, V_1-(162), V_2-(251)], m.p. 38.2° (133), 37–38° (10), 37° (29) (22), b.p. 239.5–240° at 718 mm. (134), 115.5° at 11 mm. (22) (easily volatile with steam, but not reacting with piperidine even after 8 hrs. at 100° (10)), and *4-chloro-3-nitrotoluene* [Beil. V-329, V_2-(252)], m.p. 7° (135), 5.8° (133), b.p. 260° at 745 mm. (135), 118° at 11 mm. (22) (reacts readily with piperidine at 100° (10)); e.g., $\bar{C}$ added in 2 equal portions to 3 wt. pts. HNO_3 (D = 1.5) at 0° gives 88% yield of mixt. contg. 58.8% 4-chloro-2-nitrotoluene + 41.2% 4-chloro-3-

[C̄ on pyrolysis over red-hot Pt yields (63) mainly 4,4′-dichlorodibenzyl (1,2-*bis*-(*p*-chlorophenyl)ethane [Beil. V-600, V_1-(281), V_2-(507)], colorless lfts. from alc., m.p. 112°, accompanied by a very small amt. 4,4′-dichlorostilbene (1,2-*bis*-(*p*-chlorophenyl)ethylene) [Beil. V_1-(304), V_2-(539)], ndls. from alc., m.p. 170°.]

[C̄ with H_2 in pres. of $Pd/CaCO_3$ (64) or reduced Ni (65) in alc./alk. soln. loses all its halogen as HCl; C̄ with Na in liq. NH_3 as directed (66) yields toluene and other prods.; C̄ with HI + P in s.t. at 302° for 5 hrs. gives (80% yield (67)) toluene.]

C̄ on oxidn. with 3 pts. $KMnO_4$ in dil. aq. soln. under reflux for 4–5 hrs. (68) (51), or with CrO_3 (42), or with dil. HNO_3, e.g., with 6 pts. of dil. HNO_3 (1 vol. conc. HNO_3 + 2 vols. aq.) at 145° for 1½ hrs. (69) or at 115–120° for 5–6 hrs. (70), yields *p*-chlorobenzoic acid (3:4940), m.p. 243° (for use in quant. estn. of C̄ in pres. of toluene, benzyl chloride, and *o*-chlorotoluene see (70)). — Note that with HNO_3 C̄ is more rapidly oxidized than *o*-chlorotoluene, *m*-chlorotoluene, or the various dichlorotoluenes but more slowly than *p*-bromotoluene (69). — C̄ on oxidn. with air at 260° in pres. of Na_2CO_3 and under press. (71), or on vapor-phase oxidn. over suitable cat. (72), or on electrolytic oxidn. in dil. Na_2CO_3 soln. at 60° (73) cf. (74), or even on very long stdg. (2 years) with I_2 + aq. in sunlight (75) gives *p*-chlorobenzoic acid. — C̄ with N_2O_4 yields (76) *p*-chlorobenzoic acid accompanied by nitration prods.

[C̄ with chromyl chloride (CrO_2Cl_2) yields an addn. prod. which with aq. gives in good yield (77) *p*-chlorobenzaldehyde (3:0765). — C̄ with air in aq. susp. of FeO.OH + cat. at 235–240° and 50–60 atm. press. gives (78) a mixt. of *p*-chlorobenzaldehyde (3:0765) + *p*-chlorobenzoic acid (3:4940).]

[C̄ with Cl_2 or on htg with $PbCl_4.2NH_4Cl$ or with SO_2Cl_2 in pres. of dibenzoyl peroxide in dark yields *p*-chlorobenzyl chloride (3:0220), q.v. for relevant refs. — C̄ with 2 moles Cl_2 in pres. of 5% PCl_5 at 160–170° gives (79) (80) *p*-chlorobenzal (di)chloride (3:6700). — *C̄ with 3 moles Cl_2 at high temp. in u.v. light (81) cf. (82) or with 3 moles Cl_2 (83) in pres.* of $FeCl_3$ (84) or of PCl_5 (85) (86) gives (93% yield (85)) *p*-chlorobenzotrichloride (3:6825) q.v. — C̄ with Cl_2 (1 mole) in pres. of 1% Fe or 40% $PbCl_2$ at 20° gives (65% yield (87)) a mixt. comprising 58.4% 2,4-dichlorotoluene (3:6290) + 41.6% 3,4-dichlorotoluene (3:6355).]

[C̄ with Br_2 at 130° (88) or at 160° (89) (90) or in pres. of dibenzoyl peroxide in dark at 100° (91) gives (21% yield (90)) exclusively (91) *p*-chlorobenzyl bromide [Beil. V-307, V_2-(239)], cryst. from MeOH, m.p. 62–63° (88), ndls. from 85% alc., m.p. 50° (90), 51° (79), 48.5° (89); for study of rate of side-chain bromination of C̄ in CS_2 at 57° see (92). — C̄ with 2 moles Br_2 in pres. of $BeBr_2$ (93) or in AcOH + fumg. HNO_3 + fumg. H_2SO_4 (94) gives *p*-chlorobenzal (di)bromide, m.p. 99° (93).]

[C̄ with $AlCl_3$ + HCl gas as directed (25) undergoes partial rearr. to both *o*-chlorotoluene (3:8245) and *m*-chlorotoluene (3:8275); for anal. of mixts. of the three isomers see (25).]

[C̄ with AcCl (95) or better Ac_2O (96) (97) + $AlCl_3$ in CS_2 (98) gives (yields: 85% in 4 hrs. (97), 65% (98), 34% in 2 hrs. (96)) 2-chloro-5-methylacetophenone [Beil. VII-307], b.p. 245.8–246.0° at 760.1 mm. (96), n_D^{25} = 1.5419 (96). — C̄ with β-chloropropionyl chloride (3:5690) + $AlCl_3$ in CS_2 gives (87% yield (99)) (100) 4-chloro-3-(β-chloropropionyl)toluene, oil, which on ring closure with conc. H_2SO_4 gives (72% yield (99)) (100) 7-chloro-4-methylindanone-1, cryst. from MeOH, m.p. 128° (99) (100). — C̄ with trichloroacetonitrile + $AlCl_3$ (4 moles) at 80–90° satd. with HCl gas for 2 days gives only 5% yield (101) of a mixt. of 2-chloro-5-methyl- and 5-chloro-2-methyl-ω,ω,ω-trichloroacetophenones.]

[C̄ with oxalyl (di)chloride (3:5060) + $AlCl_3$ in CS_2 for 20 hrs. at room temp. gives (40% yield (102)) 2-chloro-5-methylbenzoic acid (6-chloro-3-methylbenzoic acid) (3:4615), cryst. from aq., m.p. 163–166° (102), accompanied by some dichlorodimethyl-benzophenone, m.p. 70°, whose structure was not detd. — C̄ with fumaryl (di)chloride (3:5875) + $AlCl_3$

in CS_2 at 50–60° for 2 hrs. gives (25% yield (103)) *bis*-1,2-(2-chloro-5-methylbenzoyl)-ethylene, pale yel. cryst. from alc., m.p. 158° (103).]

[$\bar{C}$ with benzoyl chloride + $AlCl_3$ in CS_2 gives (50% yield (98)) (104) (105) 2-chloro-5-methylbenzophenone (6-chloro-3-methylbenzophenone) [Beil. VII_1-(235)], cryst. from AcOH, m.p. 35–36° (98) (104) (105), together with 5-chloro-2-methyl-(3-chloro-6-methyl)-benzophenone [Beil. VII_1-(235)], oil, b p. 210° at 30 mm. (106). — $\bar{C}$ with *o*-chlorobenzoyl chloride (3:6640) + $AlCl_3$ in CS_2 gives (106) 5,2′-dichloro-2-methylbenzophenone [Beil. VII_1-(235)], oil, b.p. 225° at 12 mm. (106).]

[$\bar{C}$ with phthalic anhydride (1:0725) + $AlCl_3$ gives (62.5% yield on the phthalic anhydride (107)) *o*-(2-chloro-5-methylbenzoyl)benzoic acid, ndls. from C_6H_6, m p. 164–165° (107), 165° (108), which with conc. H_2SO_4 at 75° for 4 hrs. (108) or with 8 pts. fumg. H_2SO_4 (20% SO_3) (107) ring-closes to give (yields: 93% (107), 85% (108)) 1-chloro-4-methyl-anthraquinone [Beil. VII-809, VII_1-(421)], yel. ndls. from AcOH or alc., m.p. 164° (107) (108). — Note that the structure of the above keto acid, m.p. 164–165°, has been definitely established (109) as shown and that it is *not* the isomeric *o*-(5-chloro-2-methylbenzoyl)-benzoic acid, which appears to be still unreported — For reactn. of $\bar{C}$ with 3,6-dichlorophthalic anhydride (3:4860) (110) or with pyromellitic anhydride (111) in pres. of $AlCl_3$ see indic. refs.]

[$\bar{C}$ does *not* (112) react with *bis*-(chloromethyl) ether (3:5245), but $\bar{C}$ with formalin + conc. HCl yields (62) 4-chloro-3-(chloromethyl)toluene since on reductn. with Zn + NaOH the prod gives 4-chloro-1,3-dimethylbenzene (3:8665). — $\bar{C}$ with aq. vapor + CO over suitable cat at 300–400° yields (113) *p*-toluic acid (1:0795). — $\bar{C}$ with NH_3 + CO over suitable cat. as directed (114) yields *p*-toluidine (see also below). — $\bar{C}$ with S_2Cl_2 + $AlCl_3$ in CS_2 gives (115) 4,5-dichloro-1,8-dimethylthianthrene, m.p. 195–197° (115).]

[$\bar{C}$ with Li in ether gives (63% yield (116)) *p*-tolyllithium; $\bar{C}$ with Li at 150° followed by treatment with aq. gives (117) toluene + 4,4′-dimethylbiphenyl. — $\bar{C}$ with Na in C_6H_6 treated with CO_2 at ord. temp. (118) (119) or at 50° and 500 lbs. press. (120) cf. (121) gives (yields: 95% (120), 76% (121)) *p*-toluic acid (1·0795), m.p. 178°. — $\bar{C}$ with Na treated with benzophenone as directed (122) yields diphenyl-*p*-tolyl-carbinol [Beil. VI-722, VI_1-(355)], m p. 72–73°.]

[$\bar{C}$ on hydrolysis with aq. vapor over silica gel contg 3% finely divided Ni at 380° (123), or with aq. vapor over cat. at 480° (124), or with aq. Na_2CO_3 in pres. of Cu at 300° under press. (125), or with 15–20% aq. NaOH at 300° (126) gives (80% yield (123)) *p*-cresol (1·1410). Note, however, claim (127) that $\bar{C}$ when hydrolyzed with 15% aq. NaOH in pres. of Cu for 2 hrs. at 315–320° yields prod. contg. not only *p*-cresol (1:1410) but also *m*-cresol (1·1730) (for extensive study of hydrolysis of $\bar{C}$ as means of prepn. of *m*-cresol see (147)). — $\bar{C}$ with H_2S at 700° over suitable cat. yields (128) thio-*p*-cresol (*p*-tolyl-mercaptan).]

[$\bar{C}$ with aq. NH_4OH + CuO at 150–250° under press. (129) or $\bar{C}$ + aq. NH_4OH + Cu salts + various anti acids at 225–230° under press. (130) (131) yields *p*-toluidine and/or di-*p*-tolylamine. — $\bar{C}$ with KNH_2 in liq. NH_3 (132) or Na in liq. NH_3 (66) yields *p* toluidine. — Note that $\bar{C}$ does not react with aq. sodium sulfanilate + Na_2CO_3 (dif. from benzyl chloride (3:8535) and use in sepn. of $\bar{C}$ from latter (8)).]

[$\bar{C}$ on mononitration yields a mixt. contg both *4-chloro-2-nitrotoluene* [Beil. V-327, V_1-(162), V_2-(251)], m.p 38.2° (133), 37–38° (10), 37° (29) (22), b.p. 239 5–240° at 718 mm. (134), 115.5° at 11 mm. (22) (easily volatile with steam, but not reacting with piperidine even after 8 hrs at 100° (10)), and *4-chloro-3-nitrotoluene* [Beil. V-329, V_2-(252)], m p. 7° (135), 5.8° (133), b p. 260° at 745 mm. (135), 118° at 11 mm. (22) (reacts readily with piperidine at 100° (10)); e g., $\bar{C}$ added in 2 equal portions to 3 wt. pts HNO_3 (D = 1.5) at 0° gives 88% yield of mixt. contg. 58 8% 4-chloro-2-nitrotoluene + 41.2% 4-chloro-3-

1934). (73)
Am. Electro-
). Silberrad,
(77) Law,
nt. 1930, II
2186: French 676,826, Feb. 27, 1930, *Cent* **1930,** I 3881. (79) Shoesmith, Slater, *J. Chem. Soc.* **1926,** 218–219 (80) McEwen, *Org. Syntheses,* Coll. Vol. 2 (1st ed.), 133–135 (1943); **12,** 12–14 (1933).

(81) Maryott, Hobbs, Gross, *J. Am. Chem Soc.* **62,** 2321 (1940). (82) Kenner, Witham, *J. Chem. Soc.* **97,** 1963 (1910). (83) Britton (to Dow Chem. Co.), U.S. 1,878,463, Sept. 20, 1932;

5, 1931, *Cent* **1931,** II 908.

(101) Houben, Fischer, *Ber.* **64,** 2648–2649 (1931). (102) Scholl, Meyer, Keller, *Ann.* **513,** 98 (1934). (103) Conant, Lutz, *J. Am. Chem. Soc.* **47,** 891 (1925). (104) Heller, *Ber.* **46,** 1500–501 (1913). (105) de Diesbach, Dobbelmann, *Helv. Chim. Acta* **14,** 374 (1931). (106) A.G.F.A., ier 267,271, Nov. 12, 1913, *Cent* **1913,** II 2014. (107) Heller, Schülke, *Ber.* **41,** 3634–3635 1908). (108) Dougherty, Gleason, *J. Am. Chem. Soc.* **52,** 1025, 1027 (1930). (109) Reilly, Drumm, *J. Chem. Soc* **1927,** 2814. (110) Keimatsu, Hirano, Yoshimi, *J. Pharm. Soc. Japan* **50,** 5–98 (1930), Cent **1930,** II 2384.

(111) de Diesbach, Schmidt, *Helv Chim. Acta* **7,** 650 (1924). (112) Stephen, Short, Gladding, *. Chem Soc.* **117,** 513 (1920) (113) Dieterle, Eschenbach, Ger. 537,610, Nov. 6, 1931, *Cent.* **932,** I 1156–1157. (114) Dieterle, Eschenbach, *Arch Pharm.* **265,** 195 (1927). (115) Ray, *J. Chem. Soc* **119,** 1963–1964 (1921) (116) Gilman, Zoellner, Selby, *J. Am. Chem Soc* **55,** 1255 1933) (117) Spencer, Price, *J. Chem. Soc.* **97,** 388 (1910). (118) I.G., French 736,428, Nov. 23, 1932, *Cent.* **1933,** II 2193 (119) I.G., Austrian 148,984, Mar. 25, 1937; *Cent.* **1937,** II 1082.

leral Phosphorus Co., Brit. 370,774,

(131) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; *Cent.* **1934,** II 1846. (132) Bergstrom eman,
van den Arend r. **19,**
2435–2440 (18 erson,
J. Chem Soc –1266
(1905). (138) iedler,
Ber. **46,** 2118–

(141) Wynne, *J. Chem. Soc.* **61,** 1078–1082 (1892). (142) Wynne, Bruce, *J. Chem. Soc.* **73,**

760–762, 772–773 (1898). (143) Vogt, Henninger, *Ann.* **165**, 363–365 (1873). (144) DeRoode, *Am. Chem*
6, 1921; S
Huntress,
38, 254–261 (1946).

3:8290 ETHYL β-CHLOROPROPIONATE

$C_5H_9O_2Cl$ Beil. II - 250

$ClCH_2.CH_2.CO.O.C_2H_5$ II_1-(111)

II_2-(227)

B.P. 162–163° at 765 mm. (1)	D_4^{20} = 1.1086 (5)	n_D^{20} = 1.42537 (5)
162.5° at 761 mm. (2)	1.1025 (18)	1.4269 (18)
162–163° at 760 mm. (3)		
162° (4)	D_4^{15} = 1.1141 (2)	n_D^{15} = 1.4284 (2)
161.4–161.8° at 758 mm. (5)		
161° (6)		
80° at 29 mm. (2)		
61.5° at 15 mm. (7)		

[For prepn. of C̄ from β-chloropropionic acid (3:0460) by esterification with EtOH + HCl (59% yield (6)) (4) or H_2SO_4 (1) see indicated refs.; from β-chloropropionyl chloride (3:5690) + EtOH see (1); from acrylic acid chloride (3:7153) + EtOH see (4) (7); from ethyl acrylate (1:3071) + HCl see (2); from acrylonitrile + HCl *to* β-chloropropionitrile followed by reactn. with EtOH see (8); from ethyl lactate (1:3303) + $SOCl_2$ + pyridine (95% yield (9)) see (9).]

C̄ with 20% alc. NaOH at room temp. (10) or htd. at 95–100° with 10 pts. conc H_2SO_4 (11) gives (90% yield (10)) *ethyl acrylate (1:3071), b.p. 101°.*

C̄ refluxed with NaI in acetone gives (yield: 81% (12), 75–80% (13)) ethyl β-iodopropionate, b.p. 183–185° at 760 mm. (13). [For study of rate of reactn. with KI in acetone see (6).] [Note also that β-iodopropionic acid with alc. HCl (as in its esterification) gives some ethyl β-chloropropionate *(14).*]

C̄ on catalytic hydrogenation as specified (7) takes up only a little H_2 [dif. from ethyl α-chloropropionate which gives quant. ethyl propionate].

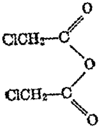
[For reactns. of C̄ with CH_3MgI (15), C_2H_5MgBr (16), and other RMgX cpds. (17) see indicated refs.]

(1885). (2) Moureu,
Chem. Soc. **1934**, 1539.
d. Sci. Fennicae **A-10**,
243, 249 (1924). (7)
, Aug. 6, 1931; *Cent.* **1931**, II 2658. (9) Darzen, *Compt. rend.* **152**, 1601 (1911). (10) Rohn, Haas, Ger. 546,141, March 12, 1932; *Cent.* **1932**, I 2642.

(11) Brit. 351,518, July 23, 1931; *Cent.* **1931**, II 1923. (12) Baker, *J. Chem. Soc.* **1933**, 216. (13) Borsche, *Ann.* **526**, 16 (1936). (14) Flürscheim, *J. prakt. Chem.* (2) **68**, 346 (1903). (15) Bennett, Philip, *J. Chem. Soc.* **1928**, 1937–1942. (16) Moureu, Barrett, *Bull. soc. chim.* (4) **29**, 994–996 (1921). (17) Weizmann, Bergmann, *J. Chem. Soc.* **1936**, 401–402. (18) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

3:0730 CHLOROACETIC ACID ANHYDRIDE $C_4H_4O_3Cl_2$

Beil. II - 199
II_1-(89)
II_2-(193)



M.P. 48–49° (16)	B.P. 163°	at 116 mm. (4)	$D_4^{50} = 1.3604$ (5)
46–47° (1)	161°	at 104 mm. (4)	$D_4^{20} = 1.5497$ (5)
46° (2)	149°	at 62 mm. (4)	
45.2° (3)	144°	at 51 mm. (4)	
	135°	at 36 mm. (4)	
	126–128°	at 30 mm. (5)	
	126°	at 24 mm. (4)	
	115–120°	at 20 mm. (6)	
	109–110°	at 10 mm. (2)	
	108–110°	at 10 mm. (16)	

Note that the above name of C̄ is so rendered to emphasize that it is the anhydride of chloroacetic acid (not a monochlorinated acetic anhydride).

Pr. from C_6H_6; eas sol. cold ether, $CHCl_3$; spar. sol. cold C_6H_6; insol. cold lgr.

[For prepn of C̄ from chloroacetic acid (3:1370) with P_2O_5 in vac. (2), or with Ac_2O (5) (6) (in latter case note also formn. of mixed anhydride acetic-chloroacetic anhydride, b.p. 80–83° at 30 mm. (5), 80–85° at 20 mm. (3), $D_4^{20} = 1.2003$ (5)), or with chloroacetyl chloride (3 5235) + an inorg acid chloride (7) or $AlCl_3$ (8), see indic. refs.; for prepn. of C̄ from sodium chloroacetate with oxalyl (di)chloride (3:5060) in C_6H_6 (54% yield) see (9); for prepn. of C̄ from chloroacetyl chloride (3:5235) with Na_2CO_3 (4) or KNO_3 (1) see indic. refs]

C̄ with aq K_2CO_3 yields (2) polyglycolide (1:4976), m.p. 220°.

[For reactn. of C̄ with $AlCl_3$ + toluene giving 46–59% ω-chloro-*p*-methylacetophenone (3:1130) see (10); for reactn. of C̄ with $AlCl_3$ + biphenyl giving 41% yield ω-chloro-*p*-phenylacetophenone, pale yel ndls. from dil. alc , m.p. 122–123° see (11); for abnormal reactn. of C̄ with benzyl MgCl yielding ω-chloro-*o*-methylacetophenone (3:9660) see (12).]

[For behavior of C̄ with various carbohydrates (13) and with cellulose (14) see indic. refs.]

C̄ htd. 4 hrs. at 160–180° with phenyl isothiocyanate yields (15) after distn. at 14–20 mm. 2,4-dioxo-3-phenylthiazolidine [Beil. XXVII-238, $XXVII_1$-(305)], m p. 147–148° (15).]

C̄ with aq hydrolyzes almost instantly yielding chloroacetic acid (3:1370). — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see chloroacetic acid (3:1370).

3:0730 (1) Diels, Okada, *Ber.* **44**, 3335 (1911). (2) Bischoff, Walden, *Ber.* **27**, 2949 (1894). (3) Watson, Gregory, *J Chem. Soc.* **1929**, 1375. (4) Patterson, *Ber.* **38**, 210–213 (1905). (5) Baroni, *Gazz. chim. ital.* **63**, 29–30 (1933). (6) Clarke, Malm (to Eastman Kodak Co.), U.S. 1,648,540, Nov. 8, 1927; *Cent.* **1928**, I 1459; *C.A.* **22**, 433 (1928). (7) Salmoiraghi, Italian 290,541, June 17, 1930, *Cent.* **1937**, I 185. (8) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929, *Cent.* **1929**, II 1215; *C.A.* **23**, 3234–3235 (1929). (9) Adams, Uhch, *J. Am. Chem. Soc.* **42**, 607 (1920). (10) Noller, Adams, *J. Am. Chem. Soc.* **46**, 1892–1893 (1924).

(11) Silver, Lowy, *J. Am. Chem. Soc.* **56**, 2429–2430 (1934). (12) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 656 (1932). (13) Brass, Kurz, *Cellulosechem.* **15**, 99–102 (1934). (14) Soc. Chem. Ind. Basel, French 764,308, May 18, 1934; *Cent.* **1935**, I 650. (15) Dubsky, *Ber.* **50**, 1690–1691 (1917). (16) Ballaus, *Monatsh.* **74**, 91 (1943).

3:8307 ETHYL *d,l*-α-CHLORO-*n*-BUTYRATE $C_6H_{11}O_2Cl$ Beil. II-277

$CH_3.CH_2.CH(Cl).COOC_2H_5$ II_1—

II_2—

B.P. 163–164° at 760 mm. (1) D^{13}_{-} = 1.056 (1) n^{-}_{-} = 1.42430 (1)

156–160° (2) $D^{17.5}_{-}$ = 1.063 (2)

[For prepn. of $\bar{C}$ from α-chloro-*n*-butyronitrile with EtOH (2) or with EtOH + HCl (1) see indic. refs.; for formn. of $\bar{C}$ from ethyl *n*-butyrate (1:3127) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (10% $\bar{C}$ + 50% β- and 40% γ-isomers (3)) see (3).]

[For use of $\bar{C}$ in Reformatsky reactn. see (4).]

For the amide corresp. to $\bar{C}$ see α-chloro-*n*-butyric acid (3:9130).

3:8307 (1) Henry, *Bull. acad. roy. Belg.* (3) **35**, 507–520 (1898); *Cent.* **1898**, I 273. (2) Markownikow, *Ann.* **153**, 241 (1870). (3) Price, Schwarcz, *J. Am. Chem. Soc.* **62**, 2894–2895 (1940). (4) Nieuwland, Daly, *J. Am. Chem. Soc.* **53**, 1842–1846 (1931).

3:8310 γ-CHLORO-*n*-PROPYL ACETATE $C_5H_9O_2Cl$ Beil. II —

(1-Acetoxy-3-chloropropane; trimethylene chlorohydrin acetate) $ClCH_2.CH_2.CH_2.O.CO.CH_3$ II_1-(58) VI - 1281 II_2-(139)

B.P. 165–166° (1) D^{21}_{4} = 1.1105 (7) n^{21}_{D} = 1.431 (7)

168–173° (2)

163–165° at 747 mm. (3)

160–166° (4)

88–90° at 22 mm. (5)

66° at 14 mm. (6)

62–63° at 10 mm. (7)

3:8295 *n*-PROPYL CHLOROACETATE $C_5H_9O_2Cl$ Beil. II - 198

n-$C_3H_7O.CO.CH_2Cl$ II_1-(89)

II_2—

B.P. 162.9° (1)		D_4^{20} = **1.1033** (6)	n_D^{20} = **1.4261** (6)
162.8–163.2° (2)		**1.1050** (2)	**1.4256** (2)
162.3–162.5° at 777.5 mm. (3)			
161–162° at 765 mm. (4)			
161° at 740 mm. (5)			

3:8295 (1) Cheng, *Z. physik. Chem.* **B-24**, 307 (1934). (2) Drushel, Hill, *Am. J. Sci.* (4) **30**, 72–78 (1910); *C.A.* **4**, 2438 (1910). (3) Schiff, *Z. physik. Chem.* **1**, 378 (1887). (4) Henry, *Compt. rend.* **100**, 115 (1885). (5) Schreiner, *Ann.* **197**, 8 (1879). (6) Schjanberg, *Z. physik. Chem.* **A-172**, 228 (1935).

3:8300 2,3-DICHLOROHEXANE $C_6H_{12}Cl_2$ Beil. I - 144

I_1—

I_2-(100)

$$CH_3.CH_2.CH_2-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$$

B.P. 162–165° (1) D_{11}^{11} = **1.0527** (1)

[For prepn. of $\bar{C}$ from 2,3-epoxyhexane with PCl_5 see (1) (2).]

$\bar{C}$ is not attacked by solid KOH but with alc. KOH yields (1) a chlorohexane, b.p. 122° (1).

3:8300 (1) Henry, *Bull. soc. chim.* (2) **41**, 363 (1884). (2) Henry, *Compt. rend.* **97**, 262 (1883).

3:8305 *d,l*-β-METHYL-*n*-CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. II —

(*sec.*-Amyl-(2)-acetyl chloride) II_1—

II_2-(298)

$$CH_3.CH_2.CH_2.\underset{CH_3}{CH}.CH_2.\underset{Cl}{C}{=}O$$

B.P. 163–164° at 751 mm. (1) D_4^{20} = **0.967** (1)

159–161° at 733 mm. (2)

[For prepn. of $\bar{C}$ from methyl-*n*-propyl-acetic acid [Beil. II_1-(146)] (1) (2) with PCl_3 (1) or $SOCl_2$ (87% yield (2)) see indic. refs.]

[$\bar{C}$ with *n*-propyl zinc iodide in toluene gives (70% yield (2)) 6-methylnonanone-4, b.p. 192–193° at 715 mm. (2).]

$\bar{C}$ on hydrolysis yields (1) β-methyl-*n*-caproic acid, [Beil. II_1-(146)] (1) (2), b.p. 215–216° (3), 212–213° at 755 mm. (1), 207–209° u.c. at 728 mm. (2).

Ⓓ β-Methyl-*n*-caproamide: m.p. 97° (1), 99° (4). [From $\bar{C}$ + excess conc. aq. NH_4OH (1).]

3:8305 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* **33**, 496–497 (1924). (2) Karrer, Shibata, Wettstein, Jacubowicz, *Helv. Chim. Acta* **13**, 1302–1303 (1930). (3) Ciamician, Silber, *Ber.* **46**, 3080 (1913). (4) Bayer & Co., Ger. 228,667, Nov. 15, 1910; *Cent.* **1910**, II 1789.

$D_4^{20} = 1.0884$, $n_D^{20} = 1.4579$ (9); cf. behavior of stereoisomeric ethyl β-chlorocrotonate (3:8538).]

C̄ with hydrazine hydrate in abs. alc. splits out HCl and EtOH with consequent ring closure yielding (18) 5-methylpyrazolone-3 [Beil. XXIV-19, $XXIV_1$-(189)], m.p. 215° (18); note that same prod. is also obtd. from *methyl* β-chloroisocrotonate (3:8028).

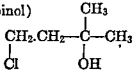
C̄ (1 mole) with phenylhydrazine (1 mole) at 100° for 6–8 hrs. gives by ring closure mainly (4) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, $XXIV_1$-(190)], pr. from aq., m.p. 127°, accompanied by small amts. of 4-benzeneazo-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, $XXIV_1$-(319)], m.p. 155–156°, and 3,3'-dimethyl-1,1'-diphenyl-*bis* pyrazolone-5,5' [Beil. XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2–4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) prods. is greatly increased (4).

3:8325 (1) Kohlrausch, Pongratz, *Z. physik. Chem.* **27**, 193 (1934). (2) Geuther, Frolich, *Zeit. für Chemie* **1869**, 273. (3) Eisenlohr, *Ber.* **44**, 3208 (1911). (4) Autenrieth, *Ber.* **29**, 1654–1664 (1896). (5) Koll, *Ann.* **249**, 323–324 (1888). (6) Lauer, Kilburn, *J. Am. Chem. Soc.* **59**, 2587 (1937). (7) von Auwers, *Ber.* **56**, 724 (1923). (8) von Auwers, *Ber.* **45**, 2807–2808 (1912). (9) Gidvani, Kon, Wright, *J. Chem. Soc.* **1932**, 1034–1035. (10) Errera, Lepingle, *Bull. sci. acad. roy. Belg.* (5) **11**, 150–153 (1925); *Cent.* **1925**, II 897; *C.A.* **19**, 3057 (1925).

(11) von Auwers, *Ann.* **432**, 62 (1923). (12) Scheibler, Voss, *Ber.* **53**, 381–382, 387–388 (1920). (13) Thomas-Mamert, *Bull. soc. chim.* (3) **13**, 70–71 (1895). (14) Scheibler, Bube, *Ber.* **48**, 1449–1451 (1915). (15) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) **124**, 7–12 (1930). (16) Ruhemann, Wragg, *J. Chem. Soc.* **79**, 1190 (1901). (17) Fichter, Schwab, *Ann.* **348**, 251–256 (1906). (18) Freri, *Gazz. chim. ital.* **66**, 25 (1936); *Cent.* **1936**, II 621; *C.A.* **30**, 6387 (1936).

3:8335 4-CHLORO-2-METHYLBUTANOL-2 $C_5H_{11}OCl$ Beil. I - 390

(β-Chloroethyl-dimethyl-carbinol) I_1— I_2-(424)



B.P. 166° (1)
72° at 13 mm. (2)
62–63° at 14 mm. (3)

[For prepn. of C̄ from methyl β-chloropropionate (3:5765) (3) or from ethyl β-chloropropionate (3:8290) (1) (53% yield (2)) with MeMgBr see indic. refs.]

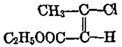
C̄ with fumg. HCl at room temp. yields (1) 2,4-dichloro-2-methylbutane (3:8105).

C̄ mixed with 3 pts. dry powdered KOH and htd. at 130–180° gives (43% yield (2)) by loss of HCl and ring closure 2,4-epoxy-2-methylbutane (α,α-dimethyltrimethylene oxide), b.p. 71° at 750 mm., $D_4^{20} = 0.8279$ (2).

C̄ with specially dried K phthalimide htd. in a s.t. 8 hrs. at 169°, finally 3½ hrs. at 218°, yields (3) (by metathesis and loss of H_2O) *N*-(2-methylbuten-2-yl-4)phthalimide, m.p. 99° (3).

3:8335 (1) Henry, *Bull. soc. chim. Belg.* **20**, 152–156 (1906); *Cent.* **1906**, II 1178; *Compt. rend.* **142**, 133 (1906). (2) Bennett, Philip, *J. Chem. Soc.* **1928**, 1938. (3) Späth, Spitzy, *Ber.* **58**, 2276–2277 (1925).

3:8325 ETHYL β-CHLOROISOCROTONATE $C_6H_9O_2Cl$ Beil. II - 417
II₁-(190)
II₂-(397)



B.P.		B.P. (*contd*)			
165.6–167.2°	(1)	60° at 15 mm.	(7)	D_4^{20} = 1.088	(8)
164°	(13)	56–57° at 13 mm.	(8) (9)	1.087	(7)
161.4°	(2)	54° at 14 mm.	(10)	1.086	(11)
159–161°	(3)	50° at 10 mm.	(11)	n_D^{20} = 1.4538	(7)
157–158° at 740 mm.	(4)			$D_4^{18.7}$ = 1.0924	(3)
155–156°	(5)			$n_D^{18.7}$ = 1.45423	(3)
154–157°	(6)			$D_4^{17.7}$ = 1.0896	(8)
				$n_D^{17.7}$ = 1.45467	(8)
				$D_4^{14.4}$ = 1.0920	(11)

[*See also ethyl β-chlorocrotonate* (3:8538).]

Note the lack of accord regarding the b.p. of C̄ especially at ordinary pressures; this is presumably attributable to more or less contamination with the stereoisomeric ester (3:8538).

[For prepn. of C̄ from β-chloroisocrotonic acid (3:1300) in EtOH with dry HCl gas (yields: 100% (4), 65% (12)) (2) (5) or a little conc. H_2SO_4 (yield 65% (6)) (8) (11) see indic. refs.]

[For prepn. of C̄ from ethyl acetoacetate (1·1710) with PCl_5 in C_6H_6 followed by refluxing with a little I_2 see (13) (1); note, however, that this method has subsequently (6) been regarded as unsatisfactory for the prepn. of pure C̄ although it suffices to give (40–50% yields (14)) a mixt. of C̄ with its stereoisomer (3:8538) which for many purposes is adequate.]

[C̄ (2 moles) with K_2S (1½ moles) in 5 vols. abs. EtOH refluxed for 5 hrs. (note that the stereoisomer (3:8538) requires 16) gives (53% yield (14)) diethyl β,β′-thiodicrotonate, $S(—C(CH_3)=CH.COOC_2H_5)_2$, b.p. 150–153° at 4 mm. (14), accompanied by some ethyl β-mercaptocrotonate (see below).]

[C̄ with alc. NaSH as directed gives (55–60% yield crude prod. (15)) ethyl β-mercaptocrotonate, note that this prod. is apparently a mixt. of the two geom. stereoisomeric thioenols together with the keto form, viz., ethyl thioacetoacetate, CH_3 CS.CH_2.$COOC_2H_5$; for details see (15); note also that ethyl β-chlorocrotonate (3:8538) by the same treatment gives the same result so that a mixt. of the esters can be employed as initial material.]

[C̄ with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl β-substituted crotonates: e.g., C̄ with NaOEt in ether gives (5) ethyl β-ethoxycrotonate [Beil. III-373, III₁-(135), III₂-(254)], m p. 29.5° (5); C̄ with Na allylate gives (6) ethyl β-allyloxycrotonate; C̄ with Na cinnamylate gives (6) ethyl β-cinnamyloxycrotonate; C̄ with Na phenolate gives (16) ethyl β-phenoxycrotonate, b.p. 152° at 18 mm. (16); note that in the three preceding cases either C̄ or its stereoisomer (3:8538) yields the same result.]

[C̄ with Na salt of ethyl mercaptan gives (12) ethyl β-ethylmercaptoisocrotonate, b.p. 127–129° at 16 mm. (12); C̄ with Na salt of benzyl mercaptan gives (75% yield (12)) a mixt. of ethyl β-benzylmercaptocrotonate, m.p. 64.5° (12), and ethyl β-benzylmercaptoisocrotonate (consts. not given).]

[C̄ with diethyl sodiomalonate gives (9) cf. (17) *cis* diethyl α-carbethoxy-β-methylglutaconate, $(C_2H_5OOC)_2CH.C(CH_3)=CH.COOC_2H_5$ [Beil. II-853], b p. 164–165° at 12 mm.,

3:8346 2-CHLORO-OCTENE-1 $CH_3—(CH_2)_5—C(Cl)═CH_2$ $C_8H_{15}Cl$ Beil. I-221, I_1—, I_2—

B.P. 168–170° (1) $D_0^0 = 0.9274$ (2)
167–168° (2)

[For prepn. of C̄ from (β-chloro-β-n-hexylvinyl)arsonic acid by htg. at 175° (1) or from octanone-2 (1:5490) with PCl_5 (2) see indic. refs.]

[Note that the structure of C̄ has *not* been unequivocally demonstrated, and it may be 2-chloro-octene-2 (3:8345).]

3:8346 (1) Fusco, Cottignoli, *Farm. ital.* **11**, 89–91 (1943); *Cent.* **1943**, II 2285; *C.A.* **38**, 6054 (1944). (2) Béhal, *Ann. chim.* (6) **15**, 277–278 (1888).

3:8350 *sec.*-BUTYL CHLOROACETATE $CH_3.CH_2.CH(CH_3).O.CO.CH_2Cl$ $C_6H_{11}O_2Cl$ Beil. S.N. 160

B.P. 167.5° at 760 mm. (2) $D_{20}^{20} = 1.062$ (2) $n_D^{19} = 1.4251$ (1)
163–164° (1) $D_{15}^{15} = 1.055$ (1)

[For prepn. from butene-2 + chloroacetic ac. (3:1370) + $ZnCl_2$ see (1).]
[For study of insecticidal action of vapor of C̄ see (2).]

3:8350 (1) Aldoschin, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1385–1389 (1938); *Cent.* **1939**, II 2223; *C.A.* **33**, 4194 (1939). (2) Roark, Cotton, *Ind. Eng. Chem.* **20**, 512–514 (1928).

3:8355 *d,l*-γ-METHYL-*n*-CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. S.N. 162
$CH_3.CH_2.CH(CH_3).CH_2.CH_2.C(Cl){=}O$

B.P. 167–168° at 767 mm. (1) $D_4^{20} = 0.9677$ (1)

[For prepn. of C̄ from γ-methyl-*n*-caproic acid (1:1136) with PCl_3 see (1).] [The dextrorotatory isomer of C̄, b.p. 80° at 50 mm. (2), has been prepared from the dextrorotatory acid + $SOCl_2$.]

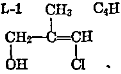
C̄ on hydrolysis yields γ-methyl-*n*-caproic acid (1:1136) q.v. (for the amide, anilide, and other derivatives corresponding to C̄ see 1:1136).

3:8355 (1) Dewael, Weckering, *Bull. soc. chim. Belg.* **33**, 501–502 (1924). (2) Levene, Rothen, Marker, *J. Biol. Chem.* **115**, 261–262 (1936).

3:8360 *d,l*-1,4-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I —, I_1—, I_2-(101)
$ClCH_2—CH_2—CH(CH_3)—CH_2Cl$

B.P. 168–169° at 760 mm. (calcd.) (1) $D_4^{24.5} = 1.1003$ (1) $n_D^{21} = 1.4562$ (1)
170–172° (2)
101–102° at 100 mm. (1)
67–69° at 18–20 mm. (3)

3:8340 3-CHLORO-2-METHYLPROPEN-2-OL-1 C_4H_7OCl **Beil. I-443**
(γ-Chloro-β-methyl-allyl alcohol) I_1— I_2—



High-boilg. (*cis ?*)
B.P.
167–167.5° (1) — D_4^{25} = **1.1262 (2)** n_D^{20} = **1.4730 (2)**
166–168° cor. (2)
163–164° (3) — D_4^{20} = **1.1243 (1)** n_C^{20} = **1.4677 (1)**

Low-boilg. (*trans ?*)
B.P.
160–162° cor. (2) — D_4^{25} = **1.1290 (2)** n_D^{20} = **1.4737 (2)**

[For prepn. of C̄ (mixt. of both forms) from 1,2,3-trichloro-2-methylpropane (3:5885) in 84% yield by hydrolysis with excess 5% aq. NaOH see (2) (4); for prepn. of C̄ from 1,3-dichloro-2-methylpropene-1 (3:5590) by hydrolysis with aq. alk. (4), with aq. Na_2CO_3 (3), or aq. + $CaCO_3$ (1) see indic. refs. Note that by virtue of allylic transposition 1,3-dichloro-2-methylpropene-1 (3:5590) may frequently yield derivatives of its synionic isomer, 1,1-dichloro-2-methylpropene-2 (3:7480).]

C̄ with excess AcOH + conc. HCl gives (60% yield (2)) 1-chloro-2-methylpropen-2-yl-1 acetate, b.p. 167–174° at 748 mm. (2), 176–178° at 784 mm. (1).

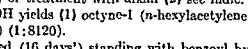
C̄ on treatment with acids as specified (5) gives 3-chloro-2-methylpropanal-1 (β-chloroisobutyraldehyde) (3:9112).

Ⓓ **1-Chloro-2-methylpropen-2-yl-1 3,5-dinitrobenzoate:** from high-boilg. form of C̄; m.p. 63.8–64.5° (2); from low-boilg. form of C̄; m.p. 94.4–95.8° (2).

Ⓓ **1-Chloro-2-methylpropen-2-yl-1 *N*-phenylcarbamate:** from high-boilg. form of C̄; m.p. 81–82° (1).

3:8340 (1) Tishchenko. *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent* **1939**, II 4223; *C.A.* **33**, 4190 (1939). (2) Rogers, Nelson, *J. Am. Chem Soc.* **58**, 1030 (1936). (3) Pogorshelski, [illegible] 31 [illegible] 1531.

3:8345 2-CHLORO-OCTENE-2 $C_8H_{15}Cl$ **Beil. I-221**
I_1— I_2-(200)



B.P. 167–168° (1) — D_{16}^{16} = **0.8923 (2)** n_D^{16} = **1.4424 (2)**

Some doubt exists as to whether this material is in fact C̄, 2-chloro-octene-1, or a mixture of both.

[For prepn. of C̄ from octanone-2 (*n*-hexyl-methyl ketone) (1:5490) with PCl_5 followed by distillation (1) or treatment with alkali (2) see indic. refs.]

C̄ with alc. KOH yields (1) octyne-1 (*n*-hexylacetylene) (1:8105) or octyne-2 (*n*-amyl-methyl-acetylene) (1:8120).

[C̄ on protracted (16 days') standing with benzoyl hydrogen peroxide in ether yields (2) 2-chloro-2,3-epoxyoctane, b.p. 81–82° at 21 mm., D_4^{16} = 0.9609, n_D^{-} = 1.4359 (2).]

3:8345 (1) Béhal, *Ann. chim.* (6) **15**, 277–278 (1888). (2) Prileshaiev, *Ber.* **59**, 197–198 (1926).

3:8373 ETHYL *d,l*-β-CHLORO-*n*-BUTYRATE $C_6H_{11}O_2Cl$ Beil. II - 277

$CH_3.CH.CH_2.COOC_2H_5$ II_1-(124)

| II_2-(253)

Cl

B.P. 169.5°	(1)	D_4^{20} = 1.0542 (6)	n_D^{20} = 1.4253	(2)
168–169°	(2)	1.0517 (3)	1.4247	(6)
168–169° at 745.4 mm.	(3)		1.42458	(3)
168–169° at 741 mm.	(4)			
65–65.5° at 15 mm.	(5)			

[For prepn. of $\bar{C}$ from ethyl *n*-butyrate (1:3127) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (50% $\bar{C}$ together with 10% α- and 40% γ-isomers) see (2); from β-chloro-*n*-butyric acid (3:0035) with EtOH + HCl see (4); from β-chloro-*n*-butyronitrile with EtOH + HCl or ethyl crotonate (1:3196) with HCl see (7) (9); from crotonic acid (1:0425) + EtOH + HCl see (3); from crotonyl chloride (3:7693) with EtOH see (8); from ethyl acetoacetate (1:1710) with Zn/Hg + alc. HCl (together with other prods.) see (10).]

$\bar{C}$ on htg. at 70–80° in s.t. with 9 vols. conc. alc. NH_3 yields (12) (13) (10) β-amino-*n*-butyramide [Beil. IV-412], sirup (chloroplatinate, pale yel. ndls. from alc., % Pt. 31.78 (10) (12)).

$\bar{C}$ on hydrolysis (e g., with aq. KOH (11)) yields EtOH (1:6130) and crotonic acid (1:0425), m.p. 72°, together with a little β-hydroxy-*n*-butyric acid.

3:8373 (1) Weidel, Roithner, *Monatsh.* **17**, 188 (1896). (2) Price, Schwarcz, *J Am. Chem. Soc.* **62**, 2894–2895 (1940). (3) Brühl, *Ann.* **203**, 27–28 (1880). (4) Balbiano, *Ber.* **10**, 1749 (1887). (5) Lovén, ... 232 (1935). (7) Henry, ... enry, *Bull. acad. roy. B*... 84). (10) Steinkopf, ...
(11) Balbiano, *Ber.* **11**, 348 (1878). (12) Balbiano, *Ber.* **13**, 312 (1880); *Gazz. chim. ital.* **10**, 137 (1880). (13) Scheibler, Magasanik, *Ber.* **48**, 1812 (1915).

3:8375 ISOBUTYL CHLOROACETATE $C_6H_{11}O_2Cl$ Beil. II - 198

$(CH_3)_2CH.CH_2O.CO.CH_2Cl$ II_1-(89)

II_2—

B.P. 170° at 760 mm. (1)	D_4^{20} = 1.0612 (2)	n_D^{20} = 1.4255 (2)
	D_4^{15} = 1.0675 (1)	

Colorless liq. with agreeable odor; insol. aq.; sol. alc., ether.

[For prepn. from isobutyl alc. (1:6165) + chloroacetic ac. (3:1370) + conc. H_2SO_4 see (1).]

For study of hydrol. by dil. aq. halogen acids see (3).

3:8375 (1) Steinlen, *Bull. acad. roy. Belg.* (3) **34**, 103 (1897); *Cent.* **1897**, II 659. (2) Schjanberg, *Z. physik. Chem.* **A-172**, 228 (1935). (3) Drushel, Hill, *Am. J. Sci.* (4) **30**, 72–78 (1910); *C.A.* **4**, 2438 (1910).

[For formn. of C̄ from 2-methylbutane (isopentane) (1:8500) with Cl_2 (together with 2,3-dichloro-2-methylbutane (3:7975) and 2,4-dichloro-2-methylbutane (3:8105)) see (3); for formn. of C̄ (together with other products) from dextrorotatory 1-chloro-2-methylbutane (*act.-amyl chloride*) by chlorination with SO_2Cl_2 + benzoyl peroxide see (1); for formn. of C̄ (together with other products) from 4-chloro-2-methylbutane (isoamyl chloride) (3:7365) + Cl_2 in light see (2).] [The dextrorotatory form of C̄ has been obtd. (4) from N,N'-dibenzoyl-2-methyltetramethylenediamine with PCl_5.]

C̄ on boilg. with AgOAc gives (3) a diacetate which upon saponification and subsequent oxidn. gives (3) methylsuccinic acid [Beil. II-637; II_1-(274)], m.p. 112°.

3:8360 (1) Brown, Kharasch, Chao, *J. Am. Chem. Soc.* **62**, 3437–3439 (1940). (2) Perkin, *J. Soc. Chem. Ind.* **31**, 616–624 (1912), *Cent.* **1912**, II (1912). (3) Davydova, Papkina, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **7**, 1992–1994 (1937); *Cent.* **1939**, I 2397; *C.A.* **32**, 482 (1938). (4) von Braun, Jostes, *Ber.* **59**, 1095–1096 (1926).

3:8365 δ-METHYL-*n*-CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. II - 342

(Isoheptanoyl chloride; isoamylacetyl chloride)

$$\underset{\displaystyle CH_3}{CH_3.\underset{|}{C}H}.CH_2.CH_2.CH_2.\underset{\displaystyle Cl}{\underset{|}{C}}{=}O$$

II_1—
II_2—

B.P. 168–169° at 739 mm. (1)

[For prepn. of C̄ from isoamylacetic acid [Beil. II-342, II_1-(146)] with PCl_3 (1) or with $SOCl_2$ (2) see indic. refs.]

[C̄ with MeOH yields methyl isoheptanoate, b.p. 166–167.5° cor. (3); C̄ with EtOH yields ethyl isoheptanoate, b.p. 181.5–182.5° cor. (3), 182.7° cor. at 750 mm (4); for reactn. of C̄ with benzyl alc., phenylethyl alc., phenylpropyl alc., geraniol, and terpineol to give corresp. esters see (5).]

C̄ on hydrolysis yields isoamylacetic acid (see above), b.p. 216° cor. at 762 mm. (4).

- Ⓓ Isoamylacet-amide: cryst. from aq., AcOEt, or CCl_4, m.p. 103° (7), 103.5–104° cor. (4), 102–103° (6).
- Ⓓ Isoamylacet-anilide: cryst. from ether + pet. ether, m.p. 74–75° (7), 75° (6).
- Ⓓ Isoamyl acet-*p*-toluidide: ndls. from dil. alc., m.p. 75° (8).

3:8365 (1) Ponzio, de Gaspari, *Gazz. chim. ital.* **28**, II 277 (1898). (2) Staudinger, Muntwyler, Kupfer, *Helv. Chim. Acta* **5**, 761 (1922). (3) Poetsch, *Ann.* **218**, 68–70 (1883). (4) Levene, Allen, *J. Biol. Chem.* **27**, 442 (1916). (5) Rothstein, *Bull. soc. chim.* (4) **53**, 1106–1107 (1938). (6) Wallach, *Ann.* **408**, 190 (1915). (7) Fournier, *Bull. soc. chim.* (4) **5**, 925 (1909). (8) Fichter, Rosenberger, *J. prakt. Chem.* (2) **74**, 324 (1906).

3:8370 *d,l*-3-(CHLOROMETHYL)HEPTANE $C_8H_{17}Cl$ *Beil. S.N. 10*

(2-Ethylhexyl chloride; 1-chloro-2-ethylhexane)

$$CH_3.CH_2.CH_2.CH_2{-}\overset{\displaystyle CH_2Cl}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}{-}CH_2.CH_3$$

B.P. 169° (1)
73° at 18 mm. (1)

[For prepn. of C̄ from 2-ethylhexanol-1 (1:6248) with $SOCl_2$ + dimethylaniline see (1).]

3:8370 (1) Weizmann, Bergmann, Haskelberg, *Chemistry & Industry* **56**, 589 (1937).

CHAPTER XIX

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:8500–3:8999)

3:8500 ***d,l*-1-CHLOROPENTANOL-3** $C_5H_{11}OCl$ Beil. I —
(β-Chloroethyl-ethyl-carbinol) I₁-(194)

$CH_3.CH_2.CH(OH).CH_2.CH_2Cl$ I_2-(421)

B.P. 173°	at 760 mm. (1)	D_4^{25} = **1.0327** (2)	n_D^{25} = **1.466** (3)
100°	at 60 mm. (1)	**1.035** (3)	**1.448** (2)
77.0–77.5°	at 20 mm. (2)		
70–71°	at 10 mm. (3)		

Liquid with weak odor resembling that of allyl alcohol. — Sparingly sol. cold aq.; sol. hot aq.

[For prepn. of C̄ from β-chloropropiona

[C̄ with AcCl yields (1) 3-acetoxy-1-chl[illegible]
4 hrs. at 160–170° with KOAc yields (4) 1-[illegible]
C̄ with BzCl yields (1) 3-benzoxy-1-chloropentane, b.p. 168° at 15 mm. (1), while C htd. to 180° for 10 hrs. with NaOBz + KI yields (4) 1-benzoxypentanol-3, b.p. 181° at 20 mm., 171° at 11 mm. (4).]

[For reactn. of C̄ with alk. Na_3AsO_3 see (3).]

[C̄ with $COCl_2$ yields (5) the corresp. chloroformate, b.p. 95° at 18 mm., which with excess NH_3 gives β-chloroethyl-ethyl-carbinyl carbamate, m.p. 68° (5).]

3:8500 (1) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) **25**, 366–368 (1919). (2) Lespieau, *Bull. soc. chim.* (5) **7**, 254–258 (1940); *C.A.* **34**, 5414 (1940). (3) Backer, Bolt, *Rec. trav. chim.* **54**, 70 (1935). (4) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) **27**, 554–556 (1920). (5) Puyal, Montagne, *Bull soc. chim* (4) **27**, 859 (1920).

3:8510 1-CHLORO-4-ETHYLHEXENE-3 $C_8H_{15}Cl$ Beil. I —

$CH_2(Cl).CH_2.CH{=}C(CH_2.CH_3)—CH_2.CH_3$ I_1— I_2-(201)

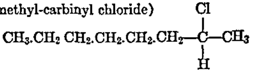
B.P. 173° (1) D_4^{20} = **0.9102** (1) n_D^{20} = **1.4524** (1)

[For prepn. of C̄ from 6-chlorohexanone-3 (γ-chloro-*n*-propyl ethyl ketone) [Beil. I_1-(355), I_2-(747)] with excess EtMgBr see (1).]

C̄ adds Br_2.

3:8510 (1) De Boosere, *Bull. soc. chim. Belg.* **32**, 35–39 (1923).

3:8378 ***d,l*-2-CHLORO-OCTANE** $C_8H_{17}Cl$ Beil. I - 160
(*n*-Hexyl-methyl-carbinyl chloride) I_1—
I_2-(124)



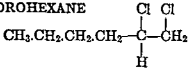
B.P. 171–173° cor. (1) $D_{25}^{25} = 0.86388$ (1)
169–171° (2)
55–56° at 14 mm. (3) $D_{15}^{15} = 0.87075$ (1)

[For prepn of $\bar{C}$ from octanol-2 (*n*-hexyl-methyl-carbinol) (1:6245) with HCl (4) (5), with PCl_5 (4) (6), or with $SOCl_2$ in pyridine (3) see indic. refs.; for prepn. of $\bar{C}$ from octene-1 + HCl + $AlCl_3$ see (7).] [The large amt. of work on the opt. act. isomers of $\bar{C}$ cannot be discussed here; see Beil. I_1-(60), I_2-(124) and subsequent literature incl. (8).]

[For study of rate of reactn. of $\bar{C}$ with KI in acetone see (2).]

3:8378 (1) Perkin, *J prakt. Chem.* (2) **31**, 495 (1885). (2) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (3) McKenzie, Tudhope, *J. Biol. Chem.* **62**, 554 (1924/25). (4) Bouis, *Ann.* **92**, 398 (1854). (5) Malbot, *Bull. soc. chim.* (3) **3**, 69 (1890). (6) Dachauer, *Ann.* **106**, 270 (1858). (7) Webb (to Carbide and Carbon Chem. Corp), U S. 1,560,625, Nov. 10, 1925, *Cent.* **1926**, I 1713, *C.A* **20**, 51 (1926). (8) Gerrard, *J. Chem. Soc.* **1944**, 85–90, **1945**, 106–112.

3:8380 ***d,l*-1,2-DICHLOROHEXANE** $C_6H_{12}Cl_2$ Beil. I -144
I_1—
I_2—

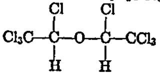


B.P. 172–174° (1) $D_{-}^{15} = 1.085$ (1)

[For prepn. of $\bar{C}$ from hexene-1 (1:8255) + Cl_2 see (1).]

3:8380 (1) Brochet, *Bull. soc. chim.* (3) **7**, 569 (1892).

3:0738 *α,α′,β,β,β,β′,β′-β′*-**OCTACHLORODIETHYL ETHER** $C_4H_2OCl_8$ Beil. I - 624
(*bis*-(*α,β,β,β*-tetrachloroethyl) ether) I_1—
I_2-(681)



M.P. 47° (1) **B.P. 130–131° at 11 mm.** (1)
45–46° (1) *128–130° at 9 mm.* (1)
40–42° (2)

Cryst. with agreeable camphoraceous odor from MeOH or EtOH. — Eas. sol. MeOH, C_6H_6, toluene, or pet. ether; spar. sol. in abs. alc. below 0°.

$\bar{C}$ slowly sublimes but on attempted distn. at ord. press. decomposes at about 240°.

[For prepn. of $\bar{C}$ from chloral (3:5210), chloral hydrate (3:1270), or metachloral with $ClSO_3H$ or FSO_3H at not above 50–60° see (1); note that from chloral (3:5210) with $ClSO_3H$ at −50° for 10–12 hrs. yield of $\bar{C}$ may be as high as 50%; from metachloral with $ClSO_3H$ at 50° for a few hrs. yield is 60% (1); note also that various other products including chloralide (3:3510) are also formed. — For formn. of $\bar{C}$ from trichloroethylene (3:5170) with excess Cl_2O in CCl_4 at −20° (2), or perhaps from *α,α′*-dichlorodiethyl ether (3:7595) with Cl_2 in sunlight (3), see indic. refs.]

$\bar{C}$ on htg. in pres. of air gives (2) phosgene (3:5000).

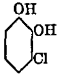
$\bar{C}$ on reduction with conc. HI ($D = 1.78$) in boilg. AcOH quantitatively yields (2) ethane.

$\bar{C}$ is fairly stable toward boilg. aq. or aq. alkalies (1).

$\bar{C}$ is claimed (1) to react with 2 moles of RMgX cpds. of either aliphatic or aromatic types, but no details are reported.

3:0738 (1) Fuchs, Katscher, *Ber.* **62**, 2381–2386 (1929). (2) Goldschmidt, Schussler, *Ber.* **58**, 569–570 (1925). (3) Roth, *Ber.* **8**, 1017–1018 (1875).

3:0745 3-CHLOROCATECHOL $C_6H_5O_2Cl$ Beil. VI —
(3-Chloropyrocatechol) VI_1-(388)
VI_2—



M.P. 47° (1) **B.P. 110–111° at 11 mm.** (2).
46–48° (2)

White cryst. (from pet. ether) (1); hygroscopic scales (from lgr.) (2). — Eas. deliquesces absorbing ½ mole H_2O. — Eas. sol. aq. but insol. almost all org. solvents except cold pet. ether or cold lgr.

[For prepn. from catechol (1,2-dihydroxybenzene) (1:1520) by action of SO_2Cl_2 in ether at 0° see (1) (2); for prepn. from *o*-benzoquinone [Beil. VII-600] by action of ethereal HCl see (2); 4-chlorocatechol (3:2470) is also a by-product of both methods.]

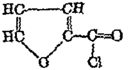
[$\bar{C}$ on oxidn. with PbO_2 in pet. ether gives (12% yield (2)) 3-chloro-*o*-benzoquinone [Beil. VII_1-(338)]; for use in prepn. of *α*-chlorophenazine see (1).]

$\bar{C}$ with $FeCl_3$ gives a blue-green color, changing to clear red on addn. of Na_2CO_3 (2).

Ⓓ **3-Chloropyrocatechol dibenzoate:** ndls. from alc., m.p. 108–109° (2); 109° u.c. (1).

3:0745 (1) Wrede, Mühlroth, *Ber.* **63**, 1932–1933 (1930). (2) Willstätter, Müller, *Ber.* **44**, 2184–2189 (1911).

3:8515 FUROYL CHLORIDE (Pyromucyl chloride; furan 2-carboxylic acid chloride)



$C_5H_3O_2Cl$ Beil. XVIII-276 XVIII₁—

B.P. 173–174°	(1)	M.P. −2° (8)
173°	(2) (3)	
170°	(4)	
58° at 12 mm.	(5)	
66° at 10 mm.	(6)	
59.5–61.5° at 7 mm.	(7)	

Colorless strongly refractive liquid rapidly decomposed in strong light (7).—C̄ is stronger lachrymator than BzCl (2).

[For prepn. of C̄ from furoic acid (1:0475) with PCl_5 (poor yields (3) (4) (6)), with excess PCl_5 in dry $CHCl_3$ as specified (100% yield (6)) (8), with PCl_3 (77% yield (5)), with $SOCl_2$ (100% (2), 79% (1), 60% (3)), with $SOCl_2$ in C_6H_6 (89.5% yield (7)), or with phosgene (9) see indic refs.]

[C̄ with MeOH yields methyl furoate (1:3452), b.p. 180.5° at 750 mm., 76° at 20 mm., $D_4^{20} = 1.1792$, $n_D^{20} = 1.4875$ (10); C̄ with EtOH yields ethyl furoate (1:2082), b.p. 197°, m.p. 34°; C̄ with furfuryl alc. (1:6425) yields (11) furfuryl furoate, dimorphous cryst., m.p. 27.5° and 19.5°, b.p. 122° at 2 mm. (11); for study of reactn. of C̄ with cellulose see (12).]

[C̄ with phenol yields (2) phenyl furoate, m.p. 41.5° (2).]

[C̄ with C_6H_6 + $AlCl_3$ yields (13) (14) α-furyl phenyl ketone [Beil. XVII-348; XVII₁-(186)], b.p. 282–284°; C̄ with toluene + $AlCl_3$ gives (80% yield (15)) α-furyl *p*-tolyl ketone, m.p. 41–42°, b.p. 180–183° at 23 mm. (15).]

[For study of reactn. of C̄ with Cl_2 (16) or Br_2 (17) see indic. refs.]

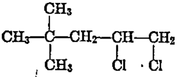
C̄ with pyridine in ether or C̄ with Na or Ag furoate yields (18) furoic anhydride, ndls. from alc., m.p. 73° (18).

C̄ on hydrolysis (*rate of reactn. even with boilg. aq. slower than BzCl* (6)) *yields furoic* acid (1:0475), m.p. 133–134° (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see 1:0475).

3:8515 (1) Bogert, Stull, *J. Am. Chem. Soc.* **48**, 252 (1925). (2) Baum, *Ber.* **37**, 2951 (1904). (3) Gelissen, van Roon, *Rec. trav. chim.* **43**, 361 (1924). (4) Liès-Bodart, *Ann.* **100**, 327 (1856); *Compt. rend.* **43**, 393 (1856). (5) Reichstein, Morsman, *Helv. Chim. Acta* **17**, 1122 (1934). (6) Frankland, Aston, *J. Chem. Soc.* **79**, 516–517 (1901). (7) Hartmann, Dickey, *Ind. Eng. Chem.* **24**, 151–152 (1932). (8) Chavanne, *Compt. rend.* **134**, 1439 (1902). (9) Meuser (to Dominion Rubber Co.), Canadian 373,516, May 3, 1938; *Cent.* **1938**, II 3609; *C.A.* **32**, 5003 (1938). (10) Price, Chapin, Goldman, Krebs, Shafer, *J. Am. Chem. Soc.* **63**, 1859 (1941).

(11) Zanetti, *J. Am. Chem. Soc.* **47**, 1452–1453 (1925). (12) Kobe, Montonna, *J. Am. Chem. Soc.* **53**, 1889–1891 (1931). (13) Marquis, *Bull. soc. chim.* (3) **23**, 33 (1900); *Ann. chim.* (8) **4**, 276–277 (1905). (14) Gilman, Hewlett, *Iowa State Coll. J. Sci.* **4**, 27–33 (1929); *Cent.* **1931**, II 1428; *C.A.* **24**, 1640 (1930). (15) Borsche, Leditsche, *Ann.* **529**, 110 (1937). (16) Hewlett, *Iowa State Coll. J. Sci.* **6**, 439–445 (1932); *Cent.* **1933**, I 942; *C.A.* **27**, 979–980 (1933). (17) Shepard, Winslow, Johnson, *J. Am. Chem. Soc.* **52**, 2083–2090 (1930). (18) Baum, *Ber.* **34**, 2505 (1901).

3:8516 *d,l*-4,5-DICHLORO-2,2-DIMETHYLPENTANE $C_7H_{14}Cl_2$ Beil. S.N. 10
(1,2-Dichloro-4,4-dimethylpentane)



B.P. 173–175° at 745 mm. (1) D_4^{20} = **1.0259** (1) n_D^{20} = **1.4489** (1)
58–59° at 12 mm. (1)

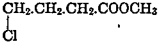
[For prepn. of C̄ from allyl chloride (3:7035) with 2-methylpropane (isobutane) + $AlCl_3$ at −10° (13–15% yield accompanied by 35–40% yield of 5-chloro-2,3-dimethylpentane (3:8153)), *or with ter-butyl chloride (3:7045) + $AlCl_3$ at −10° to −20°, see (1).*]

[C̄ with isobutane + $AlCl_3$ gives (1) a mixt. of products including *ter*-butyl chloride (3:7045), 5-chloro-2,3-dimethylpentane (3:8153), etc.]

C̄ with Zn dust + alc. reacts only very slowly under reflux but in s.t. at 120° gives (45% yield (1)) 4,4-dimethylpentene-1 (1:8285), b.p. 71.8° (1).

3:8516 (1) Schmerling, *J. Am. Chem. Soc.* **67**, 1438–1441 (1945).

3:8517 METHYL γ-CHLORO-*n*-BUTYRATE $C_5H_9O_2Cl$ Beil. II-278
II₁—
II₂—



B.P. 175–176° at 764 mm. (1) D_-^{14} = **1.1268** (1) n_D^{20} = **1.4324** (4)
173–174° (2)
172–174° at 749 mm. (3) D_-^{10} = **1.1894** (2)
102–105° at 58 mm. (3)
90° at 45 mm. (4)
55–56° at 7 mm. (5)

[For prepn. of C̄ from γ-chloro-*n*-butyronitrile with MeOH + HCl (80% yield (4)) (2) see indic. refs.; from γ-methoxy-*n*-butyric acid (3) by htg. with $SOCl_2$ for 6 hrs. (86% yield (3)) or by htg. γ-methoxy-*n*-butyryl chloride (84% yield (3)) see (3); from γ-hydroxy-*n*-butyronitrile with MeOH + HCl see (5).]

C̄ on 48-hr. reflux with alc. KOH gives (67.5% yield (3)) γ-butyrolactone (1:5070), b.p. 206°.

[C̄ refluxed 8 hrs. with NaI in acetone gives (3) methyl γ-iodo-*n*-butyrate, b.p. 80–83° at 11 mm. (3); C̄ with 4 moles MeMgCl in ether yields (4) 5-chloro-2-methylpentanol-2.]

C̄ on hydrolysis by boilg. 6 hrs. with conc. HCl gives (32% yield (3)) γ-chloro-*n*-butyric acid (3:0020) q.v.

For the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see γ-chloro-*n*-butyric acid (3:0020).

...nry,
...41).
..., 75,
339 (1942).

3:8518 ETHYL *d,l*-α-CHLORO-α-METHYL-*n*-BUTYRATE $C_7H_{13}O_2Cl$ Beil. **II-306**, II_1—, II_2—

$$CH_3.CH_2\text{—}\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}COOC_2H_5$$

B.P. 175° at 747 mm. (1) D_{-}^{14} = **1.069 (1)** n_{-}^{11} = **1.43683 (1)**

Oily liq.; insol. aq.; sol. alc., ether.
[For prepn. of $\bar{C}$ from α-chloro-α-methyl-*n*-butyronitrile with EtOH + HCl see (1).]
For the corresp. acid, α-chloro-α-methyl-*n*-butyric acid see 3:8718.

3:8518 (1) Servais, *Rec. trav. chim.* **20**, 60 (1901).

3:8520 *n*-HEPTANOYL CHLORIDE $CH_3(CH_2)_5.\underset{\underset{Cl}{|}}{C}{=}O$ $C_7H_{13}OCl$ Beil. **II-340**, II_1—, II_2—
(Enanthoyl chloride)

B.P.		F.P.		
175.2° at 760 mm.	**(1)**	**−83.8° (1)**	D_4^{25} = **0.95694 (1)**	
175.0°	**(2)**			
174–175°	**(3)**		D_4^{20} = **0.96170 (1)**	
77° at 23 mm.	**(4)**			
74–75° at 19 mm.	**(5)**		D_4^{15} = **0.96645 (1)**	n_D^{15} = **1.43447 (2)**
59–61° at 11 mm.	**(6)**		**0.9669 (2)**	
56° at 8 mm.	**(7)**			

[For prepn. of $\bar{C}$ from heptanoic acid (enanthic acid) (1:1140) with PCl_5 (2) (51% yield (8)), with PCl_3 (75% yield (1)), with $PCl_3 + ZnCl_2$ (89% yield (8)), or with $SOCl_2$ (yield 98 5% (6), 80% (8)) see indic. refs.]

[For reactn. of $\bar{C}$ with various higher alcohols see (9), with various acylureas see (10), with vanillylamine see (11) (5), with sodium *n*-heptylate to yield *n*-heptylic anhydride (1:1165), b p. 258°, see (1) (2).]

[$\bar{C}$ with $AlCl_3$ + phenol yields (12) 48% *o*-(*n*-heptanoyl)phenol, b.p. 172–174° at 20 mm. (13), 155–156° at 10 mm. (12), m.p. 24° (13), +9 8° (12), D_{-}^{24} = 1.0110 (12), $n_D^{25\,5}$ = 1.5209 (12) (phenylhydrazone, m.p. 91–92° (13), semicarbazone, m.p. 162° (12)), and 41% *p*-(*n*-heptanoyl)phenol, m.p. 93–94° (13), 91–91.5° (12), b p. 220° at 15 mm. (13) (acetate, m p 46 5° (12), benzoate, m.p. 96.5–97° (12), 92–93° (13)).]

[$\bar{C}$ on warming with NaN_3 in C_6H_6 yields (14) *n*-hexyl isocyanate, b.p. 163–164° (14), and/or (15) *n*-hexylamine HCl + *N,N'*-di-*n*-hexylurea, m.p. 58–59° (15).]

[$\bar{C}$ in ether treated with diazomethane as directed (7) yields 1-chlorooctanone-2, b.p. 91–96° at 10 mm. (7)]

$\bar{C}$ on hydrolysis yields *n*-heptanoic (enanthic) acid (1:1140) q.v. (for the amine, anilide, *p*-toluidide, and other derivatives corresp. to $\bar{C}$ see 1:1140).

3:8520 (1) Deffet, *Bull soc. chim. Belg.* **40**, 389–394 (1931). (2) Lumsden, *J. Chem. Soc.* **87**, 92–93 (1905). (3) Freundler, *Bull. soc chim.* (3) **13**, 833 (1895). (4) Krafft, *Ber.* **19**, 2987 (1886). (5) Ford-Moore, Phillips, *Rec. trav chim.* **53**, 855 (1934) (6) Fierz-David, Kuster, *Helv Chim. Acta* **22**, 86–89 (1939). (7) Spath, Lorenz, *Ber* **74**, 599–603 (1941) (8) Clark, Bell, *Trans. Roy Soc Can* (3) **27**, III 97–103 (1933). (9) Rothstein, *Bull. soc. chim.* (4) **53**, 1106–1107 (1933). (10) Stoughton, *J Org. Chem.* **2**, 514–521 (1938).

(11) Nelson, *J Am. Chem Soc.* **41**, 2124 (1919) (12) Sandulesco, Girard, *Bull. soc. chim.* (4) **47**, 1305–1310 (1930). (13) Coulthard, Marshall, Pyman, *J. Chem. Soc.* **1930**, 280–291. (14) Schroeter, *Ber.* **42**, 3358 (1909). (15) Nelles, *Ber.* **65**, 1346–1347 (1932).

3:8523 ETHYL α-CHLOROCROTONATE $C_6H_9O_2Cl$ Beil. II - 415, II_1-(189), II_2-(395)

$$CH_3-C-H \quad \| \quad Cl-C-COOC_2H_5$$

B.P.		B.P. (*contd.*)			
176–178°	(1)	85° at 35 mm.	(3)	$D_4^{20.1} = 1.1086$ (8)	
175–177°	(2)	67–68° at 15 mm.	(2)		$n_D^{20.1} = 1.45303$ (8)
176° at 760 mm.	(3)	72° at 14 mm.	(8)	$D_4^{20} = 1.109$ (8)	
176°	(4)	61° at 10 mm.	(9)	1.102 (9)	
175–176° cor.	(5)			$D_4^{19.8} = 1.1133$ (6)	
175.0–175.5°	(6)				$n_D^{19.8} = 1.45378$ (6)
				$D_4^{14.3} = 1.1073$ (9)	

[*See also ethyl α-chloroisocrotonate* (3:9368).]

[For prepn. of $\bar{C}$ from α-chlorocrotonic acid (3:2760) in EtOH with dry HCl gas (4) (5) (8) or with conc. H_2SO_4 (9) see indic. refs.; from α-chloroisocrotonic acid (3:1615) in EtOH with conc. H_2SO_4 at 100° (note isomerization) see (9); from the ethyl ester of the lower-melting (63°) α,β-dichloro-*n*-butyric acid (3:1375) in EtOH with KCN (1 mole) for 10 min. (75% yield) see (3); from ethyl α,α,β-trichloro-*n*-butyrate (3:6380) with Zn in moist ether (100% yield) see (10); from α,α,β-trichloro-*n*-butyraldehyde (butylchloral) (3:5910) (1) as hydrate (3) or cyanohydrin (3) in EtOH with KCN (2 moles) below 15° (85% yield (3)) see indic. refs.; from ethyl α-chloro-α-vinylacetate (2) by isomerization of the double bond with NaOAc/AcOH under reflux 30–40 hrs. see (2).]

[$\bar{C}$ with Al/Hg in alc. gives (11) crotonic acid (1:0425), m.p. 72°.]

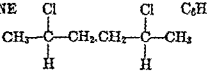
$\bar{C}$ with diazomethane in dry ether does not react (12); however, upon addn. of a drop of water addition of CH_2N_2 to unsatd. linkage takes place with elimination of HCl (on distillation) yielding (12) ethyl 4-methylpyrazole-3-(5)carboxylate [Beil. XXV-117], m.p. 156–157° (12).

[$\bar{C}$ with piperidine (3 moles) in abs. alc. stood 3 hrs. then neutralized, etc., (13) gives (by reactn. of 1 piperidine with the halogen and addition of a second molecule of piperidine to the unsatd. linkage (or vice versa)) (63% yield (13)) ethyl α,β-di-piperidino-*n*-butyrate, viscous oil, insol. aq., b.p. 181–183° at 14 mm.]

3:8523 (1) Wallach, *Ann.* **173,** 301 (1874). (2) Rambaud, *Bull. soc. chim.* (5) **1,** 1353–1354 (1934). (3) Chattaway, Irving, *J. Chem Soc.* **1929,** 1043–1045. (4) Sarnow, *Ann.* **164,** 101 (1872). (5) Perkin, *J. Chem. Soc.* **65,** 424 (1894). (6) Eisenlohr, *Ber.* **44,** 3208 (1911). (7) Roberts, *J. Chem. Soc.* **1938,** 779. (8) von Auwers, *Ber.* **45,** 2806 (1912). (9) von Auwers, *Ann.* **432,** 61 (1923). (10) Michael, Schulthess, *J. prakt. Chem.* (2) **43,** 595 (1891).

(11) Wislicenus, *J. prakt. Chem.* (2) **54,** 59–60 (1896). (12) von Auwers, König, *Ann.* **496,** 31, 41 (1932). (13) Roberts, *J. Chem. Soc.* **1938,** 963–964.

3:8525 2,5-DICHLOROHEXANE $C_6H_{12}Cl_2$ Beil. I - 144



I_1—
I_2—

d,l-form

B.P.

176.4–177.4° cor. at 751.1 mm. (1) D_4^{25} = **1.0431** (1)

62.0–62.5° at 12 mm. (2)

D_4^{12} = **1.0529** (2) n_C^{12} = **1.4495** (2)

D_4^{0} = **1.0675** (1)

meso-form

B.P. M.P.

177.8–178.2° cor. at 751.8 mm. (1) **18.7°** (1)

D_4^{25} = **1.0459** (1)

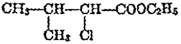
[For prepn. of $\bar{C}$ (presumably mixt. of both diastereoisomers) from hexadiene-1,5 (biallyl) (1:8045) by shaking with 5 vols. conc. HCl for 120 hrs. at room temp. (57% yield accompanied by 23% 5-chlorohexene-1 (3·7665)) see (1), from 2,5-dimethyltetrahydrofuran [Beil. XVII-14] on protracted treatment with HCl gas + $ZnCl_2$ (8% yield (3)) see (3).]

[For sepn. of *meso*- from *d,l*-form by cooling to −50° see (1).]

[For behavior of $\bar{C}$ on treatment with *N*/10 aq. alc. KOH see (2).]

3:8525 (1) Cortese, *J. Am. Chem. Soc.* **52**, 1519–1520 (1930). (2) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1380–1388 (1939); *C.A.* **34**, 1611 (1940). (3) Fried, Kleene, *J. Am. Chem. Soc.* **63**, 2691 (1941).

3:8528 ETHYL *d,l*-α-CHLORO-ISOVALERATE $C_7H_{13}O_2Cl$ Beil. II - 316
(Ethyl α-chloro-β-methyl-*n*-butyrate)



II_1—
II_2—

B.P. **177–179°** at 756 mm. (1) $D_-^{13.2}$ = **1.021** (1) n_-^{11} = **1.42951** (1)

Oil with odor like peppermint.

[For prepn. of $\bar{C}$ from α-chloro-isovaleric acid (3:0050) with EtOH + H_2SO_4 see (1); for formn. from ethyl α-diazo-isovalerate with HCl see (2).]

3:8528 (1) Servais, *Rec. trav. chim.* **20**, 54 (1901). (2) Curtius, *J. prakt. Chem.* (2) **125**, 254 (1930).

3:8530 *n*-BUTYL CHLOROACETATE $C_6H_{11}O_2Cl$ Beil. II - 198

n-$C_4H_9O.CO.CH_2Cl$

II_1—
II_2-(192)

B.P. **178.2–179°** at 727 mm. (1) D_4^{20} = **1.0704** (4) n_D^{20} = **1.4301** (4)

176.7° (2)

91° at 38 mm. (3)

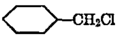
Colorless mobile liq. with fragrant odor. — Insol. aq., misc. with alc. or ether (5).

[For prepn. (97% yield (3)) from *n*-butyl alc. (1.6180) + chloroacetic ac. (3:1370) see (3).]

[For study of insecticidal action of vapor of $\bar{C}$ see (6).]

3:8530 (1) Gustus, Stevens, *J. Am. Chem. Soc.* **55**, 384–385 (1933). (2) Cheng, *Z. physik. Chem.* **B-24**, 307 (1934). (3) Liston, Dehn, *J. Am. Chem. Soc.* **60**, 1264–1265 (1938). (4) Schjånberg, *Z. physik. Chem.* **A-172**, 228 (1935). (5) Gehring, *Bull. soc. chim.* (2) **46**, 147 (1886). (6) Roark, Cotton, *Ind. Eng. Chem.* **20**, 512–514 (1928).

3:8535 BENZYL CHLORIDE (α-Chlorotoluene; ω-chlorotoluene)



C_7H_7Cl Beil. V - 292; V_1-(151); V_2-(227)

B.P.			
179.35°	at	760 mm.	(1)
179.3°	at	760 mm.	(2)
179° cor.			(3)
179°	at	749 mm.	(4)
178.6–179.0°	at	766 mm.	(5)
178.5–179°			(6)
178.5°	at	754 mm.	(7)
178.0–178.5°			(8)
177.5–178°	at	755 mm.	(142)
177.0–177.5° u.c.			(9)
175.2–178.3°			(28)
175–175.2°	at	769.3 mm.	(10)
174.0–174.8°			(28)
173° dec.			(11)
172°	at	730 mm.	(12)
141°	at	261 mm.	(13)
128°	at	163 mm.	(13)
118°	at	111 mm.	(13)
106.2°	at	92 mm.	(14)
103°	at	76.1 mm.	(14)
96–99°	at	62 mm.	(15)
100°	at	59 mm.	(13)
93.3°	at	47.8 mm.	(14)
89.9°	at	40 mm.	(14)
83.6°	at	28.64 mm.	(14)
81.5–82°	at	28 mm.	(16)
81.8°	at	26.74 mm.	(14)
78.2°	at	22.1 mm.	(14)
73.9°	at	17 mm.	(14)
66–67°	at	16 mm.	(17)
70.4–70.5°	at	15 mm.	(11)
64.0–64.2°	at	12 mm.	(18)
66°	at	11 mm.	(13)
61–62°	at	11 mm.	(19)
63.0°	at	8.2 mm.	(14)
57–58°	at	8 mm.	(20)
56–58°	at	4–5 mm.	(21)
51–52°	at	4 mm.	(22)

See also Note 1.

F.P.	
−37.5°	(23)
−39.0°	(1)
−39.2°	(24)
−39.7°	(7)
−41.2°	(25)
−43.2°	(26)
−48.0°	(27)

D_4^{30} = 1.08977 (24)
1.08815 (28)
1.08699 (28)
D_4^{25} = 1.09460 (24)
1.100 (29)
n_D^{25} = 1.5363 (21)
D_4^{20} = 1.09943 (24)
n_D^{20} = 1.5391 (31) (32)
$n_D^{17.4}$ = 1.5391 (33)
$D_4^{15.4}$ = 1.1138 (30)
$n_D^{15.4}$ = 1.5415 (30)
D_4^{15} = 1.10426 (24)
n_D^{15} = 1.54124 (24)
D_-^7 = 1.099 (34)
n_D^7 = 1.5415 (34)

See also Note 2.
See also Note 3.

Note 1. Despite an earlier report (1), C̄ is later (34) stated to decompose so readily on heating that precise detn. of boiling point at 760 mm. is impracticable.

Note 2. The presence of benzyl alc. (1:6480) lowers density; presence of HCl or of oxidation products raises density (24).

Note 3. Values of n_D^{20} for mixtures of C̄ with benzal (di)chloride (3:6327) (for which n_D^{20} = 1.5502) are linear with composition (31).

[*See also benzal (di)chloride* (3:6327) *and benzotrichloride* (3:6540).]

Colorless liq. with penetrating odor; vapor of C̄ is irritating to eyes. — Insol. aq., volatile with steam. — Insol. cold conc. H_2SO_4, but soon reacts evolving HCl. C̄ dissolves below −20° in equal vol. pet. ether (35).

Binary systems containing C̄. *C̄ + toluene:* for b.p. and vapor press. relations see (36). — *C̄ + anisole:* for f.p./composition data see (25). — *C̄ + N-methylaniline:* for f.p./composition data see (25).

C̄ with benzaldehyde (1:0195) forms a const.-boilg mixt., b.p. 177.9° at 760 mm., contg. 50 wt. % C̄ (37-a). — *C̄ with n-butyric acid* (1:1035) forms a const.-boilg. mixt , b.p. 160 8° at 760 mm , contg. 35 wt. % C̄ (38) — *C̄ with isobutyric acid* (1:1030) forms a const.-boilg. mixt , b.p. 153 5° at 760 mm , contg. 20 wt. % C̄ (38). — *C̄ with n-caproic acid* (1:1130) forms a const.-boilg mixt , b.p. 179.0° at 760 mm , contg. 97 wt. % C̄ (38).

C̄ with chloroacetic acid (3:1370) forms a const -boilg mixt., b.p. 172° at 760 mm., contg. 72 wt. % C̄ (38-b) — *C̄ with "α-dichlorohydrin"* (1,3-dichloropropanol-2) (3:5985) forms a const.-boilg. mixt , b.p. 168.9° at 760 mm., contg. 43 wt % (2)

PREPARATION OF C̄

From benzene. The prepn. of C̄ from benzene (1:7400) by direct introduction of the —CH_2Cl group (chloromethylation) has been much studied especially in recent years. Chloromethylation may be effected with paraformaldehyde (1:0080), formalin (1:0145), chloromethyl methyl ether (3.7085), or *bis*-(chloromethyl) ether (3:5245), each in the pres. of $ZnCl_2$ and frequently also of HCl gas. For a general review of the process of chloromethylation see (39) and subsequent articles (32) (40) (41). Various by-products of the reaction are formed, notably ω,ω'-dichloro-*p*-xylene (3:2825) and diphenylmethane (1:7120). For study of further chloromethylation of C̄ to various poly-(chloromethyl)-benzenes see (41).

[For prepn. of C̄ from C_6H_6 (1:7400) by chloromethylation with paraformaldehyde (1:0080) + $ZnCl_2$ + HCl (yields: 80% (42), 73 5% (40), 70% (32), 36% (42)) (39), with formalin (1:0145) + $ZnCl_2$ + HCl (yields: 70.5% (40), 57% (44)) (45) (39) (48), or with chloromethyl methyl ether (3:7085) (40) (43) (46) (47) or *bis*-(chloromethyl) ether (3:5245) (40) (43) see indic. refs.]

From toluene. [For prepn. of C̄ from toluene (1:7405) by chlorination with SO_2Cl_2 in pres. of dibenzoyl peroxide (75–80% yield (15)), with SO_2Cl_2 (for study of effect of catalysts see (83) (84)) below 130° (49) (50), with SO_2Cl_2 in pres. of acetyl chloride (51), with Cl_2 (52) (53) (for study of catalysts see (85)) in vapor phase (54) (55) (61) in light (56) (57) (58) (59) (60) (62), with Cl_2 in pres. of Pb + PCl_3 (63), with NOCl at 150° (64) or 350° (65), with NCl_3 (66), or with *ter*-butyl hypochlorite (3.7165) (62% yield (67)) see indic. refs.]

From benzyl alcohol. [For prepn. of C̄ from benzyl alcohol (1:6480) with HCl gas (68), with conc. aq HCl at 60° (70–100% yield (69)) (70) in C_6H_6 (study of kinetics at 60° (71)), with conc. HCl + $ZnCl_2$ in cold (100% yield (72)), with PCl_3 + $ZnCl_2$ (60% yield (72)), with $SOCl_2$ (100% yield (73)) in C_6H_6 (85% yield (72)) or in *N,N*-dimethylaniline (26% yield (72)), or with $AlCl_3$ in pet. eth. above 40° (74) see indic. refs.]

From other miscellaneous sources. [For formn. of C̄ from benzyl chloroformate (3:9565) on htg. (75) (76), from benzyl benzoate (1:4422) with 5 moles SO_2Cl_2 (77), from dibenzyl ether (1:7640) or other benzyl ethers with PCl_5 (78), from dibenzyl disulfide with excess SO_2Cl_2 in C_6H_6 at 37–39° (79), from benzylamine with NOCl in ether at −15° (80) or with *aqua regia* (81), or from tetrabenzylhydrazine with conc. HCl on htg. (82) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Determination of C̄. Many methods for detn. of C̄ have been employed and no complete listing can be given here; the following examples, however, may be helpful. [For detn. of C̄ by boilg. with alc. $AgNO_3$ and weighing pptd. AgCl see (85) cf. (83); for detn. of C̄ in

C_6H_6 by addn. of excess standard $AgNO_3$ in isopropyl alc., htg. several hrs., and excess $AgNO_3$ titrated with standard aq. NaCl see (71); for methods of detn. of C̄ in pres. of benzal (di)chloride (3:6327) or benzotrichloride (3:6540) see (86) (87).]

Pyrolysis of C̄. [C̄ on boiling (34) (88) gradually dec. with evoln. of HCl. — C̄ over glowing Pt wire gives (89) (90) much stilbene (1:7250) accompanied (91) by small amounts of toluene (1:7405) and dibenzyl (1:7149).]

Resinification of C̄. C̄ under the influence of various catalysts condenses with itself evolving HCl and yielding a material of composition $(C_7H_6)_n$; this material is often (though incorrectly) designated as polymeric C̄. Because of the indefinite character of the product and the voluminous and diffuse character of the literature, no exhaustive review will here be attempted. However, for extensive reviews of this reaction see (92) (93); for studies of catalysts for this type of reaction see also (94) (95) (96) (97).

Reduction of C̄. [C̄ with H_2 in pres. of $Pd/BaCO_3$ (98) or Ni (99) in alc. KOH loses all its halogen as HCl (use in quant. detn.), but the corresp. org. reduction prod. has not been characterized. — C̄ with H_2 in pres. of colloidal Pd in alc. gives (76% yield (100)) toluene (1:7405). — C̄ with EtOH + Zn dust on boilg. gives (101) cf. (102) toluene (1:7405) + benzyl ethyl ether (1:7530). — C̄ in EtOH/KOH with hydrazine hydrate in pres. of Pd boiled for 1 hr. gives (29% yield (103)) dibenzyl (1:7149); note that in conc. soln. only traces of dibenzyl are formed (103) cf. (104) and the principal prod. is *N,N*-dibenzylhydrazine [Beil. XV-533, XV_1-(164)] accompanied by some benzyl ethyl ether (1:7530).]

Oxidation of C̄. C̄ upon oxidn. yields either benzoic acid or benzaldehyde according to circumstances.

[C̄ with air at 160° over Ni cat. (105), with O_2 in u.v. light (106), or with CrO_3/H_2SO_4 at 95–98° for 1½ hrs. (note that β-chloroethylbenzene (3:8712) is stable under these conditions (107)) cf. (53), gives benzoic acid (1:0715). — C̄ with conc. aq. alk. at 250–280° and at 300–500 lb./sq. in. press. gives (80–90% yield (108)) benzoic acid (1:0715).]

[C̄ with equimolal amt. SeO_2 refluxed without solv. for 3 hrs. (109), with CrO_2Cl_2 followed by aq. (110), with hot very dil. HNO_3 (111) (112), with hot 14% aq. $Pb(NO_3)_2$ (111), with boilg. aq. $Ca(NO_3)_2$ (112), with boilg. aq. $Na_2Cr_2O_7$ + Na_2CO_3 (113), with boilg. aq. or alc. hexamethylenetetramine (114) (115), with air at 160° over Ni cat. (105), or with steam + air at 360–480° over V_2O_5 on pumice (116) (117) gives benzaldehyde (1:0195); naturally any over-oxidn. gives also some benzoic acid (1:0715).]

[Note that auto-ignition temp. of C̄ on Pt in air at ord. press. is 627° (118).]

Substitution of C̄. *Chlorination* [C̄ with NOCl at 150° gives (64) benzal (di)chloride (3:6327). — C̄ with aq. $PbCl_4.2NH_4Cl$ on boilg gives (119) benzal (di)chloride (3:6327) + benzotrichloride (3:6540). — C̄ with Cl_2 in pres. of I_2 at 30–40° gives (120) cf. (121) both *o*-chlorobenzyl chloride (3:6400) and *p*-chlorobenzyl chloride (3:0220). — Note that C̄ with Cl_2 in sunlight (122) undergoes both substitution and addition and that only isolatable prod. was benzal (di)chloride hexachloride, m.p. 153°.]

Bromination. [C̄ with Br_2 at 100° gives (123) cf. (124) a mixt. of benzyl bromide, benzal chlorobromide, and benzal (di) bromide. — C̄ with Br_2 + $BeBr_2$ in ether gives (125) *p*-bromobenzyl bromide. — C̄ with Br_2 in pres. of I_2 gives (126) (127) a mixt. of *p*-bromobenzyl bromide and *p*-bromobenzyl chloride.]

Sulfonation. [Presumably because of facile hydrolysis or resinification of C̄ with conc. H_2SO_4, its direct sulfonation has not been reported. However, *p*-sulfobenzyl chloride (ω-chlorotoluene-*p*-sulfonic acid) [Beil. XI_1-(30)] has been prepd. (e.g., (128) (129)) from sodium salt of *p*-toluenesulfonic acid by chlorination.]

Nitration. C̄ on mononitration gives a mixt. of *o*-nitrobenzyl chloride [Beil V-327, V_1-(162), V_2-(252)], m.p. 49–50° (130), 49.5° (17), 48–48.5° (131), 48–49° (132), 47.9° (133) (143), *m*-nitrobenzyl chloride [Beil. V-329, V_1-(163), V_2-(252)], m.p. 45–46° (130),

45.5° (17) (131) (134), 44.9° (143), 44.8° (133), and p-nitrobenzyl chloride [Beil. V-329, V_1-(163), V_2-(253)], cryst. from alc., m.p. 72.5° (17) (131) (134), 72.4° (133), 71–72° (130), 71.95° (143), 71° (53). — [For earlier studies of this mononitration of $\bar{C}$ see (53) (135) (136) (137) (138) (139) and especially (140). — Subsequent studies of this mononitration have been primarily concerned with the proportion of isomers; e.g., $\bar{C}$ on mononitration with conc. HNO_3 in acetic anhydride gives (133) 40.9% o-, 4.2% m-, and 54.9% p-nitrobenzyl chlorides (cf. (141) (142) (144)). — For thermal anal. of various mixtures of these three nitrobenzyl chlorides see (133) (143). — For study of rate of nitration of $\bar{C}$ in nitrobenzene soln. at 16–18° see (145). Note that p-nitrobenzyl chloride is a useful reagent for characterization of organic acids by conversion to the corresp. p-nitrobenzyl esters (146) (147); for transformation of p-nitrobenzyl chloride to p-nitrobenzyl bromide in alc. NaBr see (147) cf. (148).]

[Direct polynitration of $\bar{C}$ has not been reported; however, p-nitrobenzyl chloride on further nitration with HNO_3/H_2SO_4 as directed (149) (150) gives 2,4-dinitrobenzyl chloride [Beil. V-344, V_2-(263)], tbls. from ether, m.p. 34° (150), 33–34° (149). — No other dinitrobenzyl chlorides and no trinitrobenzyl chlorides have been reported.]

Hydrolysis of $\bar{C}$. $\bar{C}$ on hydrolysis by various means gives benzyl alcohol (1:6480) and HCl.

[$\bar{C}$ with aq. on protracted boilg. (151) (86) in sunlight (154), with steam + cat. at 550–850° (155) cf. (156), with boilg. aq. K_2CO_3 (157) or alk.-earth carbonates at elev. temps. (158) (159), with hot aq. suspension of PbO (111), with boilg. aq. Na_2CO_3, NaOH, or their mixt. (160) (161), or with anhydrous formic acid (162) gives benzyl alcohol (1:6480).— For studies on kinetics of hydrolysis of $\bar{C}$ in aq. (163) (169), in 95% EtOH at 30° and 40° (164) (165), in 50% acetone at 60° (166) cf. (167) (168) (170) (17), in dioxane (22), or in formic acid (170) see indic. refs.]

Behavior of $\bar{C}$ with Other Inorganic Reactants

With alkali sulfhydrates. [$\bar{C}$ with alc. KSH (171) (172) or aq. NaSH (173) (174) (175) gives (75% yield (172)) benzyl mercaptan [Beil. VI-453, VI_1-(224), VI_2-(427)], b.p. 194–195° (171), 99° at 32 mm (176), 75.8–76.2° at 10 mm. (11), D_4^{25} = 0.8097 (176), n_D^{25} = 1.5729 (176) (corresp. benzoate, m.p. 30° (177), 3,5-dinitrobenzoate, m.p. 119–120° (177), reaction prod. with 3-nitrophthalic anhydride, m.p. 136–137° (177), 2,4-dinitrophenyl thioether, m.p. 182.5° cor. (185)). Note that benzyl mercaptan with isotopic sulfur has been prepared (178) from $\bar{C}$ via conversion to RMgCl and reaction with S^{34}.]

With alkali sulfides. [$\bar{C}$ with alc. K_2S (171) or alc. Na_2S (179) gives (83% yield (179)) dibenzyl sulfide [Beil. VI-455, VI_1-(225), VI_2-(429)], tbls. from ether, $CHCl_3$, or alc., m.p. 49–50° (180), 49° (171) (179) (181) (corresp. sulfoxide [Beil. VI-456, VI_1-(226), VI_2-(429)], m.p. 135° (182), 133–134.6° (183), 132–133° (179); corresp. sulfone [Beil. VI-456, VI_1-(226), VI_2-(430)], m.p. 151° (184), 149.5–151° (183), 149.5–150° (179)).]

With alkali polysulfides. [$\bar{C}$ with alc. $Na_2S.9H_2O$ + S (186) (189) in C_6H_6 (187) cf. (188) gives dibenzyl disulfide [Beil. VI-465, VI_1-(229), VI_2-(437)], m.p. 74° (189), 72° (190), 71–72° (191), 70° (186) (corresp. disulfoxide [Beil. VI-466, VI_1-(230), VI_2-(438)], m.p. 108° (190) (192) cf. (209) (201) (210)).]

With salts of various sulfur acids. [$\bar{C}$ with conc. aq. K_2SO_3 (194) cf. (196) or Na_2SO_3 (195) in aq. alc. at 37° (197) (for study of rate at 40° see (16)) or at 190–200° under press. (93% yield (198)), or $\bar{C}$ with aq. Na_2SO_3/NaOH on boilg. (80% yield (199)) (192), gives corresp. salt of toluene-α-sulfonic acid (benzylsulfonic acid) [Beil. XI-116, XI_1-(32)]; for dimorphism of Na salt see (200) (corresp. sulfonyl chloride, m.p. 92–93° (201) (202), 92° (203); corresp. amide, m.p. 105° (203) (192), 104–105° (199), 102° (204); corresp. methyl ester, m.p. 61–62° (205)).]

[$\bar{C}$ with $Na_2S_2O_3$ on boilg. in aq. alc. (206) or aq. (207) gives salt of *S*-benzylthiosulfuric acid [Beil. VI-439, VI_1-(230)] (corresp. quaternary salt, viz., benzyl-dimethyl-phenyl-ammonium *S*-benzylthiosulfate, from metathesis of benzyl-dimethyl-phenyl-ammonium chloride with sodium *S*-benzylthiosulfate, has m.p. 104° (208)).]

With salts of other inorganic acids. [$\bar{C}$ with NaI in acetone (211) (212) or abs. MeOH (213), or $\bar{C}$ with KI in acetone (214) or EtOH (215), gives (90% yield (211)) benzyl iodide [Beil. V-314, V_1-(157), V_2-(241)], m.p. 24° (211) (212), 27–30° (213), b.p. 97–98° at 11 mm. (216), 93° at 10 mm. (214). — *For study of rate of reaction of $\bar{C}$ with KI in acetone at 25°* (19) (20), 30° (19), and 50° (19), or with NaI or LiI in acetone at 25° or 30° (19), see indic. refs.]

[$\bar{C}$ with powdered $AgNO_3$ in dry ether 20 hrs. in cold, then at 70–75° for 5 hrs., gives (84% yield (219)) (220) benzyl nitrate [Beil. VI-439], explosive liquid, b.p. 106° at 20 mm. (219), 100–101° at 18 mm. (21), 43° at 0.5 mm. (220). — For study of kinetics of reaction of $\bar{C}$ with solid $AgNO_3$ (221) in pres. of inert diluents such as dry ether, $CHCl_3$, and CCl_4 (222) see indic. refs.; for study of kinetics of reaction of $\bar{C}$ with $Hg(NO_3)_2$ in aq. dioxane see (21).]

[$\bar{C}$ with $AgNO_2$ (223) (224) (231) or better mercurous nitrate (225) gives ω-nitrotoluene (phenylnitromethane) [Beil. V-325, V_1-(161), V_2-(249)], b.p. 225–227° dec. (226) (227) cf. (228), 141–142° sl. dec. at 35 mm. (226), 135° at 25 mm. (229), 118–119° at 16 mm. (230), 110° at 8 mm. (231), 90–92° at 3 mm. (232); $D_4^{24.7} = 1.1540$ (233), $D_0^{20} = 1.1598$ (226); $n_{He}^{24.7} = 1.5285$ (233), $n_D^{20} = 1.5323$ (226); note, however, that phenylnitromethane is best prepd. in a different way, viz., from benzyl cyanide with methyl nitrate and alc./NaOEt (50–55% yield (232)). — Note that the isomeric benzyl nitrite [Beil. VI-439], unstable oil, b.p. 80–81° at 35 mm. (234), has been reported from benzyl alcohol (1:6480) with aq. $NaNO_2 + H_2SO_4$ (234).]

[$\bar{C}$ with NaN_3 in alc. refluxed 6 hrs. gives (90% yield (234)) ω-azidotoluene (benzyl azide) [Beil. V-350, V_1-(174), V_2-(274)], oil, insol. aq. and volatile with either steam or ether, b.p. 108° at 23 mm. (235), 82.5° at 16.5 mm. (234), 74° cor. at 11 mm. (236); $D_-^{24.9} = 1.0655$ (237); $n_D^{24.9} = 1.53414$ (237).]

[For behavior of $\bar{C}$ with metallic cyanides see below under organic acids.]

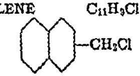
With ammonia. $\bar{C}$ with ammonia under various circumstances (see below) gives one (or more) of the following amines.

Benzylamine [Beil. XII-1013, XII_1-(445)], liq. with faint characteristic odor, misc. with aq. alc. ether: b.p. 184.5° cor. at 760 mm. (238), 184–186° cor. at 745 mm. (239), 184° at 767 mm. (240), 182° at 749 mm. (226), 181.5–182° at 740 mm. (241), 90° at 12 mm (242); $D_4^{25} = 0.9812$ (243), $D_4^{20} = 0.9822$ (244); $n_D^{20} = 1.54015$ (226), $n_D^{19.5} = 1.54406$ (244) (corresp. $\bar{B}$.HCl, m.p. 255.5–258° (245), 255–256° rap. htg. (226), 253° (246); $\bar{B}$ PkOH, m.p. 195–199° (247), 194° (248); $\bar{B}$.3,5-dinitrobenzoic acid, m.p. 210.0° cor. (249); $\bar{B}$ 2,4-dinitrobenzoic acid, m.p. 199.1–200.1° cor. (513); $\bar{B}$.*p*-toluenesulfonic acid, m.p. 180.5–181.5° u.c. (250), 180° (251)). — *Dibenzylamine* [Beil. XII-1035, XII_1-(453)], oil, insol. aq., eas. sol. alc., ether; b.p. >300° dec. (252), 268–271° cor. at 250 mm. (238), 218–220° at 60 mm. (253), 215° ± 1° at 39 mm. (254), 186° at 19 mm. (255), 172° at 14 mm. (256); f.p. −25.6° (254); $D_4^{25} = 1.024$ (255), 1.019 (257); $D_4^{21.6} = 1.0256$ (244); $n_D^{21.6} = 1.57432$ (244) (corresp. $\bar{B}$ HCl, m.p. 256° (252), 255.5° (258); $\bar{B}$.*p*-toluenesulfonic acid, m.p. 155.5–156.5° u.c. (250)). — *Tribenzylamine* [Beil. XII-1038, XII_1-(454)], solid, m.p. 92° (259) (260), 91° (256) (261) (262); b.p. 218–222° at 14 mm. (256), 230° at 13 mm. (259) (corresp. $\bar{B}$.HCl, m.p. 227–228° (263), 221° (261); $\bar{B}$.*p*-toluenesulfonic acid, m.p. 200.0–202.5° u.c. (250)).

[For formn. of mixts. of benzylamine, dibenzylamine, and tribenzylamine (properties given in preceding paragraph) from reaction of $\bar{C}$ with aq. NH_4OH at 80° for 8 days (264) or at 125° and 8 atm. press. (265) in pres. of cat. (266); from reaction of $\bar{C}$ with alc. NH_3 on

3:0747 2-(CHLOROMETHYL)NAPHTHALENE $C_{11}H_9Cl$ Beil. V - 567
V_1—
V_2-(464)

(β-Naphthylmethyl chloride;
β-menaphthyl chloride)



M.P. 48–49° (11) B.P. 170° at 20 mm. (1)
48° (1) 168° at 20 mm. (2) (6)
47.8° (2) 162° at 15 mm. (1)
47–48° (3)
47° (4) (5) (6)

[*See also* 1-(*chloromethyl*)*naphthalene* (3:0250).]

Colorless cryst. from alc. (6) (5); loses HCl on attempted distn. at ord. press.

[For prepn. of C̄ from 2-methylnaphthalene (1:7605) with Cl_2 in sunlight (5) (3) (6) and best at elevated temp., e.g. 220° (7) or even 250–280° (8) (53% yield (11)), see indic. refs.; from β-naphthylcarbinol [Beil. VI-668] (4) (2) with PCl_5 (2) or with $SOCl_2$ in toluene (4) see indic. refs.; from *N*-(benzoyl)-β-naphthylmethylamine (1) or from *N*-(benzoyl)-*bis*-(β-naphthylmethyl)amine (1) by htg with PCl_5 see (1).]

C̄ on oxidn. with aq. $Pb(NO_3)_2$ soln. yields (6) β-naphthaldehyde (1:0036); C̄ on oxidn. with alk. $KMnO_4$ yields (6) β-naphthoic acid (1:0800).

C̄ on reductn. with Zn/Cu couple yields (2) 2-methylnaphthalene (1:7605).

[C̄ with excess Na in dry ether readily gives (8) α,β-*bis*-(2-naphthylmethyl)ethane, m.p. 182° (9) (picrate, m.p. 198° (9)).] — [For study of reactn. of C̄ with 1-(chloromethyl)-naphthalene (3:0250) + $AlCl_3$ in CS_2 see (7).]

[C̄ with Mg in dry ether + trace C_2H_5I gives corresp. β-$C_{10}H_7.CH_2MgCl$, but reactn. is capricious and requires pure C̄ (4), the RMgCl cpd. with AcCl in ether does not follow a normal course but gives instead 1,3-di-(β-naphthyl)-2-methylpropene-1, cryst. from AcOH, m.p. 184–185° (4).]

[*For study of reactn. of* C̄ *with ethyl acetoacetate* + *NaOEt in abs. alc. giving* (83% yield) ethyl α-(β-naphthylmethyl)acetoacetate see (10).]

C̄ with aq. at 100° for 1½ hrs. is 17% hydrolyzed (1).

[C̄ with large excess of conc. C_6H_6 soln. of dimethylamine htd. in s.t. at 100° for 10 hrs. yields (1) *N*,*N*-dimethyl-β-naphthylmethyl-amine.]

3:0747 (1) von Braun, Moldaenke, *Ber.* **56**, 2168–2171 (1923). (2) Sah, *Rec. trav. chim.* **59**, 461–470 (1940), *C.A.* **35**, 4763 (1941). (3) Achmatowicz, Lindenfeld, *Roczniki Chem.* **18**, 69–74 (1938); *Cent.* **1939**, II 359 (4) Campbell, Anderson, Gilmore, *J. Chem. Soc.* **1940**, 820. (5) Scherler, *Ber.* **17**, 1529 (1884). (6) Schulze, *Ber* **17**, 1529 (1884). (7) Clar, Lombardi, *Gazz. chim. ital.* **62**, 542–544 (1932), *C.A.* **27**, 81 (1933). (8) Clar, Wallenstein, *Ber.* **64**, 2080, 2082 (1931). (9) Friedman, *Ber.* **49**, 1354–1355 (1916). (10) Semproni, *Gazz. chim. ital.* **68**, 263–266 (1938).
(11) Tarbell, Fukushima, Dam, *J. Am. Chem. Soc.* **67**, 198 (1945).

3:0750 1,1,2,3,4-PENTACHLOROBUTANE $C_4H_5Cl_5$ Beil. S.N. 10

(Solid diastereoisomer)
(1,2,3,4,4-Pentachlorobutane
(solid diastereoisomer))

$$CH_2(Cl)—CH(Cl)—CH(Cl)—CHCl_2$$

M.P. 49° (1) B.P. 230° (1) D_{-}^{53} = 1.530 (2) n_D^{53} = 1.5065 (2)
48° (2) 105–107° at 13 mm. (1)
102° at 11 mm. (2)

[*See also liquid diastereoisomer* (3:0068).]

gives (yields: 92% (329), 85% (212)) benzylamine (for constants see above under behavior of C̄ with NH_3) as hydrochloride; RMgCl with $BrNH_2$ gives (63% yield (330)) benzylamine. — RMgCl with NCl_3 gives (331) both benzylamine (32% yield) and dibenzylamine (7% yield). — RMgCl with SiF_4 gives (336) $(C_6H_5.CH_2)_3SiF$, m.p. 79°, accompanied by some $(C_6H_5.CH_2)_4Si$, m.p. 127.5°; the latter is also obtd. (20.7% yield (337)) from RMgCl with Na_2SiF_6.]

RMgCl with organic reactants frequently (but not invariably) leads to products derived from *o*-tolyl MgCl and/or *p*-tolyl MgCl: for reviews on and studies of this rearr. of RMgCl see (332) (333) (334) (335). — RMgCl shows little if any tendency to act as a reducing agent in Grignard additions; for review of reducing action of many Grignard reagents (including $C_6H_5.CH_2MgCl$) see (338).

[RMgCl with CO at 120° under press. gives (60% yield (339)) 1,3-diphenylpropene-1 [Beil. V-643, V_1-(310), V_2-(552)]. — RMgCl with CO_2 gives (yields: 75–76% (310), 62.7% (335), 60% (340), 51% (318), 40% (333)) phenylacetic acid (1:0665).]

[RMgCl with trioxymethylene gives (50–55% yield (341)) (342) (343) *o*-tolylcarbinol (1:5922) (*note rearr.*), but RMgCl with acetaldehyde (as paraldehyde) gives (343) (335) the expected benzyl-methyl-carbinol [Beil. VI-503, VI_1-(251), VI_2-(472)]. — RMgCl with benzaldehyde gives according to conditions various prods. including benzyl-phenyl-carbinol (1:5958) (78% yield (344)) (345) (346), stilbene (1:7250) (25–35% yield (316)), and other products.]

[RMgBr with acetone gives (347) (343) benzyl-dimethyl-carbinol (1:5910). — RMgCl gives with diphenylketone (85% yield (349)) (348) benzyl-diphenyl-carbinol [Beil. VI-721, VI_1-(354), VI_2-(696)] easily dehydrated to (54–59% overall yield (316)) α,α,β-triphenylethylene [Beil. V-722, V_1-(355), V_2-(630)].]

[RMgCl with $ClCH_2OCH_3$ (3:7085) according to circumstances gives either or both the "normal" prod. (350) (351) methyl β-phenylethyl ether [Beil. VI-479, VI_1-(238), VI_2-(449)] and the "abnormal" prod. (352) (353) methyl *o*-tolylcarbinyl ether [Beil. VI-484]. — RMgCl with $ClCH_2O.CH_2CH_3$ (3:7195) according to circumstances gives either or both the "normal" prod. (354) ethyl β-phenylethyl ether [Beil. VI_1-(450)] or the "abnormal" products (352) (332) ethyl *o*-tolyl ether [Beil. VI-484] and ethyl *p*-tolyl ether [Beil. VI-498].]

[RMgCl with methyl chloroformate (3:5075) gives some "abnormal" prod. (333). — RMgCl with ethyl chloroformate (3:7295) gives not only the "normal" tribenzylcarbinol [Beil. VI-723, VI_1-(356)] (355) and ethyl phenylacetate (1:3872) but also "abnormal" products (332) (333).]

[RMgCl with acetyl chloride (3:7065) gives (yields: 24% (333), 18% (335)) (332) the "abnormal" product, methyl *o*-tolyl ketone (*o*-methylacetophenone) (1:5224). — RMgCl with benzoyl chloride (3:6240) gives (333) the "abnormal" product, phenyl *o*-tolyl ketone [Beil. VII-439, VII_1-(234)].]

[RMgCl with benzenesulfonyl chloride gives (356) (357) benzyl phenyl sulfone [Beil. VI-455, VI_2-(428)] (2.9% yield (356)) cf. (357) and C̄ (60% yield (356)).]

RMgCl with alkyl *p*-toluenesulfonates gives hydrocarbons. — [E.g., RMgCl with methyl *p*-toluenesulfonate gives (40.9% yield (358)) ethylbenzene (1:7410), with ethyl *p*-toluenesulfonate (358) or diethyl sulfate (359) gives (yields: 100% (359), 38.3% (358)) *n*-propylbenzene (1:7450), with *n*-propyl *p*-toluenesulfonate gives (35.6% yield (358)) *n*-butylbenzene (1:7515), with *n*-butyl *p*-toluenesulfonate gives (yields: 67% (361), 50–59% (360), 24.6% (358)) *n*-amylbenzene (1:7549). — RMgCl with γ-chloro-*n*-propyl *p*-toluenesulfonate gives (42–50% yield (362)) ω-chloro-*n*-butylbenzene (δ-phenyl-*n*-butyl chloride) [Beil. V_1-(201), V_2-(317)].]

stdg. several days (268) (269) (270) or in s.t. at 100° (256) (267), with NH_3 in conc. aq. phenol in s.t. at 100° for 18 hrs. (271), with liq. NH_3 for 24 hrs. (256), or with 5 moles aq. $(NH_4)_2CO_3$ for 5–6 hrs. at 85–110° (160) see indic. refs.]

[For formn. of benzylamine from reaction of C̄ with K phthalimide at 170–180° followed by hydrolysis of the *N*-benzylphthalimide (*see below under* Ⓓ*'s*) *with fumg.* HCl at 200° for 2 hrs (272) cf. (273) (274), with silver cyanate followed by hydrolysis with alkali (275) (276) cf. (268) (277), with acetamide followed by hydrolysis with alc. KOH (278), or with hexamethylenetetramine followed by hydrolysis with alc. HCl (279) see indic. refs]

[For formn. of tribenzylamine from reaction of C̄ with $NaNH_2$ at 120° for 24 hrs. see (261) (280)]

With hydroxylamine. [C̄ with $NH_2OH.HCl + Na_2CO_3$ in aq. alc. under reflux gives (281) (282) (283) (284) *N,N*-dibenzylhydroxylamine [Beil. XV-19, XV_1-(9)], m.p. 124° (284), 123–124° (285), 123° (281); note that the isomeric *O,N*-dibenzylhydroxylamine [Beil. XV-21], oil, b.p. 145–146° at 3 mm. (286), is obtd. indirectly. — C̄ with acetone oxime refluxed in 75% AcOH *gives (287) (as the hydrochloride) N-benzylhydroxylamine [Beil.* XV-17, XV_1-(8)], m.p. 57° (288), 56–58° (289) (B̄.HCl, m.p. 110° (288)). — Various other benzylated hydroxylamines cannot be discussed here.]

With hydrazine. [C̄ with alc 50% hydrazine hydrate under reflux gives (290) *N,N*-dibenzylhydrazine [Beil. XV-533, XV_1-(164)], m p. 65° (B̄.HCl, m.p. 202° (292), 200° (290)); note that the isomeric *N,N'*-dibenzylhydrazine [Beil. XV-534, XV_1-(166)], m.p. 47° (291) (B̄ HCl, m.p. 225° (293)), is prepd. indirectly. — Various other benzylated hydrazines *cannot be discussed here.*]

With metals. *Sodium* [C̄ with Na at 30° on stdg gives (294) encrustation of $NaCH_2$-C_6H_5 [Beil. XVI_1-(589)]; the solid is wine red within 5 hrs , red-violet in 12 hrs., blue-violet in 36 hrs., and finally blue-black; and the sodium benzyl can be isolated as a blue-violet solid stable in air (294) — C̄ with Na at 100° (295) in a mixt. of C_6H_6 and toluene *(296) or in toluene (297) gives* dibenzyl (1:7149). — C̄ *with* Na in liq. NH_3 *loses its halogen* quantitatively (298) giving (50% yield (299)) dibenzyl (1:7149) accompanied by toluene and other products. — For study of free benzyl radical from C̄ with Na vapor in helium see (302)]

[C̄ with Cu powder in s.t. at 150–160° for 12 hrs (300), or C̄ with Al powder (pretreated with H_2 at 500°) *refluxed at 200° for 1 hr (301), gives (60% yield (301)) dibenzyl (1:7149).]*

Magnesium [C̄ as vapor passed over htd. Mg gives (303) magnesium allylide which with aq yields methylacetylene ("allylene").]

[C̄ with Mg in dry ether gives (304) (305) (306) C_6H_5 CH_2MgCl: for study of optimum conditions (311) giving yields of 94.28% (307), 93.2% (308), 91 0–94.1% (309), 90.7–91.2% (310) *see indic. refs.; for study of effect of nature of Mg (312), of use of* ether/hydrocarbon mixts. as solvent (313), of stability toward long boilg in ether or ether/benzene (314) see indic. refs., for further examples of practical prepn. of $C_6H_5.CH_2MgCl$ see (315) (316). — Note that some dibenzyl (1:7149) (e.g., 9.4% (317)) and di-*p*-tolyl (4,4'-dimethylbiphenyl) (318) are also formed and the yield of dibenzyl is greatly increased in pres. of cat. such as $CuCl_2$, $HgBr_2$, $FeCl_3$, $FeBr_3$ (319), *or* $MoCl_5$ (320).]

An exhaustive treatment of the behavior of $C_6H_5.CH_2MgCl$ (hereafter called RMgCl) is far beyond the scope of this book, but the following examples will be useful and will serve as lead references; for further examples see Beil. XVI-939, XVI_1-(554) and subsequent literature.

[RMgCl with O_2 gives (80% *yield (321)) cf (322) benzyl alcohol (1:6480).* — RMgCl (1 mole) gives (84% yield (323)) (324) (325) $C_6H_5CH_2HgCl$, m.p. 104° (323) (324) (326), but excess RMgCl with $HgCl_2$ gives (326) (325) (327) dibenzyl mercury, m p. 111° (326). — RMgCl with $SbCl_3$ gives (328) tribenzylstilbene, m.p. 107–108°. — RMgCl with $ClNH_2$

[$\bar{C}$ with benzyl alc./$NaOCH_2C_6H_5$ in ether (415), with solid KOH at 180–200° (416), with conc. aq. NaOH at 90–120° (416), or with K benzylate in liq. NH_3 (408) gives dibenzyl ether (1:7640).]

With phenols (or phenolates). $\bar{C}$ with phenols may react either with phenolic or nuclear hydrogen giving respectively benzyl aryl ethers or benzylated phenols; moreover, the former may, under appropriate conditions, be rearranged to the latter; examples of all these types of reaction are included below.

[$\bar{C}$ with K phenolate (111) (418) or Na phenolate (417) in boilg. alc., or $\bar{C}$ with phenol in boilg. alc. NaOMe or NaOEt (419) (420), boilg. aq. NaOH (160) (421), or boilg. acetone + K_2CO_3 (422) gives (73% yield (421)) benzyl phenyl ether [Beil. VI-432, VI_1-(220), VI_2-(411)], m.p. 39° (418) (420) (421) (422), 38–39° (401); b.p. 286–287° (401), 286–288° (419), 178–179° at 35 mm. (422), 124–125° at 4 mm. (417). — Note that although this prod. is completely stable to distn. (419) yet on htg. with $ZnCl_2$ or in dry HCl as directed (421) it undergoes rearr. (accompanied by some cleavage) giving 2-benzylphenol (1:1431), 4-benzylphenol (1:1485), 2,4-dibenzylphenol (see below), and other prods.]

$\bar{C}$ under suitable conditions also effects nuclear benzylation of phenol yielding a mixt. of *o*-benzylphenol (1:1431) and *p*-benzylphenol (1:1485) (the latter usually predominating) accompanied by polybenzylphenols and other products. [E.g., $\bar{C}$ with phenol (1:1420) directly at 125° (423) or 150–180° (160), or in pres. of Cu powder at 115–120° (160), Ce at 120–130° (424), Ti (393), $AlCl_3$ in pet. ether (425), Zn at room temp. (426) (427) (428) (429) in solvent media such as C_6H_6, toluene, $CHCl_3$, or EtOH (430), $ZnCl_2$ on warming (421) (431) (432), 38% HCl in s.t. at 100° (421), P_2O_5 (434) or PCl_5 (435) in toluene at 130–135°, or $\bar{C}$ with Na phenolate (or phenol + Na) in dry toluene (419) (436) (437) gives *o*-benzylphenol + *p*-benzylphenol (accompanied by other products). — For sepn. of the two benzylphenols by formn. of Na salt of latter in toluene see (438).]

Other phenols, cresols, naphthols, etc., behave analogously but cannot be discussed here.

With phenol ethers. With phenol ethers (where no phenolic H atom is available for reaction) $\bar{C}$ effects nuclear benzylation. [E.g., $\bar{C}$ with methyl phenyl ether (anisole) (1:7445) refluxed 2–3 hrs. (391), or in pres. of Zn (439), Ti (393), Ce (424), W (365), $AlCl_3$ (440), or $ZnCl_2$ + dry HCl (421) gives (yields: 63% (393), 57% (424), 52.9% (365)) *p*-benzylanisole [Beil. VI-676, VI_1-(325), VI_2-(630)], b.p. 305–308° (425), 191–193° at 38 mm. (391), 172–174° at 10 mm. (421), 157–158° at 8 mm. (411), 133–135° at 4 mm. (425); m.p. 20–21° (441).]

[$\bar{C}$ with phenetole (1:7485) in pres. of Ti (393), U (365), or Ce (424) as directed gives (yields: 76% (393), 80% (365), 88% (424)) *p*-benzylphenetole [Beil. VI-676, VI_2-(630)], b.p. 317° (442), 315–317° (425), 217° at 37 mm. (442), 203° at 12 mm. (442), 171–173° at 12 mm. (425).]

With organic acids (or their salts). *KCN or NaCN.* [$\bar{C}$ with alc. KCN (443) (444) (445) (446) in pres of CuCN and in u.v. light (447), or $\bar{C}$ with aq. alc NaCN (160) (448), gives (yields: 80–90% (448), 70–76% (447), 70% (160)) benzyl cyanide (α-tolunitrile) (phenylacetonitrile) [Beil. IX-441, IX_1-(176)], b.p. 233–234° cor. (3), 231–232° at 755 mm. (449), 135–140° at 38 mm. (448), 118–119° at 20 mm. (450), 107–107.4° at 12 mm. (18); f.p. −24.6° (26), −26.5° (451); $D_4^{25} = 1.0125$ (452), $D_4^{20.2} = 1.0176$ (453), 1.0157 (454); $n_D^{25} = 1.52105$ (455), $n_D^{20.2} = 1.52422$ (453); for removal from this prod. of traces of benzyl isocyanide with aq. H_2SO_4 at 60° see (456).]

With salts of aliphatic acids. [$\bar{C}$ with Na formate + anhydrous formic acid in s.t at 140° (402) gives benzyl formate (1:3596) q.v.]

[$\bar{C}$ with KOAc in alc. (443) (457) (460) or benzyl acetate itself (458), or $\bar{C}$ with $Pb(OAc)_2$ in AcOH (459), or $\bar{C}$ with NaOAc in AcOH (461) cf. (160) or aq at 115° (160), gives (80% yield (160)) benzyl acetate (1:3751) q.v.; for study of kinetics see (22).]

BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

With hydrocarbons. $\bar{C}$ with benzene (1:7400) in pres. of widely varied condensing agts. gives diphenylmethane (1.7120), frequently accompanied by *o*-dibenzylbenzene [Beil. V-710, V_1-(351), V_2-(621)], m.p 78–79°, and by *p*-dibenzylbenzene [Beil. V-711, V_1-(351), V_2-(621)], m p. 86°. — [E g , $\bar{C}$ with benzene (1·7400) in pres. of Zn dust (363) (369), Cr powder (364), uranium dust at 100° for 4 hrs. (365), Al powder (preheated in H_2 at 500°) (301), Ti (393), Al/Hg (366) (367), Al + $HgCl_2$ (368), Al + HCl (368), $AlCl_3$ (369) (370), $AlCl_3$/nitrobenzene cpd. at 30° (372), NaCl.$AlCl_3$ at 15–20° (373), $BeCl_2$ at 100° for 6 hrs. (374), $TiCl_4$ (375), $ZrCl_4$ (376), $SnCl_4$/diethyl etherate (377), $TlCl_3$ (378), iron pyrites (97), Ag_2SO_4 (379), silver methionate (neutral silver salt of methanedisulfonic acid) (379), P_2O_5 (380), or HF in Cu bomb at 100° for 15 hrs (381) gives (yields: 60–63% (368), 60% (372) (374), 56% (381), 52% (373), 49.5–52.5% (366), 40% (365), 38% (301), 35% (375), 30% (376), 22% (363)) diphenylmethane (1:7120).]

[$\bar{C}$ with toluene (1:7405) in pres. of Zn dust (382) cf. (383) (384), Ti (393), $AlCl_3$ (369) (370) cf. (385) (386) (371), Al/Hg (367), $FeCl_3$ (385) (386), $BeCl_2$ at 110–125° (374), or MeMgI (387) gives *p*-benzyltoluene [Beil V-607, V_1-(286), V_2-(511)], b.p. 279°.]

[$\bar{C}$ with *m*-xylene (1:7420) in pres. of Zn dust (388), finely divided Cu (389), or $BeCl_2$ at 130–140° (374) gives (73.6% yield (384)) phenyl-*m*-xylyl-methane [Beil. V-615, V_1-(289), V_2-(518)], b.p. 295–296° cor. (388) (389)]

[$\bar{C}$ with mesitylene (1.7455) refluxed 60 hrs. without cat. (391), or in pres. of $AlCl_3$ (390) at 98–100°, or $BeCl_2$ at 140–160° (374), gives (78% yield (374)) benzylmesitylene (phenyl-2,4,6-trimethylphenyl-methane) [Beil. V-619], m p. 36–37° (390), 36° (374)]

[$\bar{C}$ with biphenyl (1:7175) refluxed 3 hrs without cat. (391), or in pres. of Zn dust at 100° (392), or of Ti (393) gives 4-benzylbiphenyl [Beil V-708, V_2-(618)], m.p. 85° (392) (391).]

[$\bar{C}$ with naphthalene (1:7200) refluxed 3 hrs. without cat. (391), or in pres of Zn dust (394) (395), $ZnCl_2$ (396) at not over 125° (397), $AlCl_3$ (396) (398), Ti (393), or P_2O_5 at 200° (380) gives mainly 1-benzylnaphthalene [Beil. V-689, V_1-(341), V_2-(604)], m.p. 59° (corresp. picric acid addn. cpd., m p. 100–101° (396) (400)), accompanied by some 2-benzylnaphthalene [Beil. V-690], m p. 55–55.5° (398), 55 5° (399) (corresp picric acid addn. cpd., m.p. 93° (396) (400)). — Note that using $ZnCl_2$ little 2-benzylnaphthalene is formed (398), also that polybenzylation may occur (399).]

With alcohols (or alcoholates). [$\bar{C}$ with MeOH/KOH (401) or with MeOH/NaOMe (403) in s.t at 120° (402) gives benzyl methyl ether (1.7475), b.p. 170–171° cor. (403), 170 5° cor. at 760 mm. (3), 170–171° at 759 mm. (377), 170 2–172 2° at 760 mm (404); D_4^{25} = 0.9745 (405), 0 9594 (403), D_4^{20} = 0 9649 (403); n_D^{25} = 1.4983 (403), n_D^{20} = 1.5031 (405), 1.5008 (403) (corresp. picrate, m.p. 115–116° u c (406)). — $\bar{C}$ with EtOH/KOH (401), EtOH/NaOEt (403) (377) (407), EtOH/LiOEt (407), or KOEt/liq. NH_3 (408) gives (yields: 81% (408), 63–77% (407)) benzyl ethyl ether (1:7530); b.p. 184 7–185 2° at 761 mm. (377), 184–186° cor. (403); D_4^{25} = 0 9446 (403), D_4^{20} = 0.9490 (409), 0.9478 (403); n_D^{25} = 1.4934 (403), n_D^{20} = 1.4958 (403), 1 4955 (409). — For studies of rate of reaction of $\bar{C}$ with EtOH (410) (411) or with EtOH/NaOEt (412) see indic refs.]

[$\bar{C}$ with *n*-PrOH/NaO-*n*-Pr gives (90–93% yield (413) (403)) benzyl *n*-propyl ether [Beil. VI-431, VI_1-(219), VI_2-(410)], b.p. 200–202° cor. (403), 68° at 9 mm. (413); D_4^{25} = 0.9480 (403), D_4^{20} = 0 9535 (403) cf. (413); n_D^{25} = 1 4932 (403), n_D^{20} = 1.4953 (403), 1.4905 (413); for study of rate at 50 6° see (414). — $\bar{C}$ with iso-PrOH/NaOisoPr gives (403) benzyl isopropyl ether, b.p. 192–194° cor.; D_4^{25} = 0.9403, D_4^{20} = 0.9457; n_D^{25} = 1.4876, n_D^{20} = 1.4900 (403)]

[For corresp. prepn. and constants for benzyl *n*-butyl ether (403) (417), benzyl *sec*-butyl ether (417), benzyl isobutyl ether (403), and benzyl isoamyl ether (403) see indic. refs.]

[C̄ with $C_2H_5NH_2$ in 33% aq. soln. with some alc. in s.t. at 110° gives (558) *N*-ethylbenzylamine [Beil. XII-1020, XII_1-(448)], oil, spar. sol. aq., b p. 199° (539), 198° at 750 mm. (550), 194° cor. (558), 191–194° u c. at 740 mm. (548); $D_{15}^{16.7}$ = 0 9350 (552) (B̄.PkOH, m.p. 122–123° (559)), accompanied by *N*-ethyldibenzylamine [Beil. XII-1036], b p. 306° cor. (558).]

With aromatic primary amines. [C̄ (1 mole) with aniline (2 moles) in s t. at 160° for 24 hrs. (502), or htd. in open vessel at 140° (503), or in pres. of I_2 at 50° (504), in alc. (505) or aq. Na_2CO_3 (160), or C̄ (1 mole) with aniline (4 moles) in aq. $NaHCO_3$ at 90–95° (506), or C̄ with sodium anilide (from aniline + Na + Cu_2O) at 30–100° under press., (507) gives (yields: 85–87% (506), 56% (160), 49% (504)) *N*-benzylaniline (*N*-phenylbenzylamine) [Beil. XII-1023, XII_1-(449)], m.p. 39° (508), 37–38° (509), 37° (510), 36.5–36 8° cor. (503), 36 5° (511), 36° (506) (512); b p. 306–307° at 759 mm. (509), 201–203° at 37 mm. (510), 178–180° at 12 mm. (506), 171.5° at 10 mm. (508); D_4^{65} = 1.0298 (508); n_D^{65} = 1.59562 (508) (B̄.HCl, m.p. 214–216° (509), B̄.3,5-dinitrobenzoic acid, m p. 133.0° cor. (249), B̄.2,4-dinitrobenzoic acid, m.p. 121.4–122.2° cor. (513), B̄.*p*-toluenesulfonic acid, m.p. 148 3–148.8° cor. (250)); for method of sepn of *N*-benzylaniline from *N*,*N*-dibenzylaniline (below) by reactn. with phthalic anhydride (1:0725) see (514). — For studies of kinetics of reaction of C̄ with aniline in MeOH at 35° and 45° (515) or in EtOH at 35°, 40°, and 45° (516) cf. (4) see indic. refs.; for study of rearr. of *N*-benzylaniline to *p*-aminodiphenylmethane see (517)]

[C̄ with aniline on htg cf. (503) (508) in pres of NaOH at 100° (518), anhydrous NaOAc + I_2 at 97° (504), $NaNH_2$ + Cu powder (519), benzyl alc. (520), or aq. Na_2CO_3 (160) gives *N*,*N*-dibenzylaniline (*N*-phenyldibenzylamine) [Beil. XII-1037, XII_1-(453)], m.p. 71–72° *(521), 70° (522), 69.5° (508), 69° (520), 67° (518)*; b p. 226° at 10 mm. (508); D_4^{80} = *1.04436*; n_D^{80} = 1.60647 (508) (B̄.HCl, pr. with 1 H_2O from alc (518), but m.p. unreported; B̄ PkOH, m.p. 131–132° dec. (518); B̄.3,5-dinitrobenzoic acid gives no cpd. (249); B.2,4-dinitrobenzoic acid gives no cpd. (513); B̄.*p*-toluenesulfonic acid is oil (250); 2B̄.1,3,5-trinitrobenzene, m.p. 86–87° (523)). — For study of rearr. of *N*,*N*-dibenzylaniline hydrochloride to *p*-aminodiphenylmethane, 2,4-dibenzylaniline, and 2,4,6-tribenzylaniline see (524).]

C̄ with other aromatic primary amines behaves similarly but cannot be detailed here; however, for a number of cases see (508).

With aliphatic secondary amines. [C̄ with $(CH_3)_2NH$ in abs. alc. on stdg. (560) or under reflux (546) (561), or in C_6H_6 at 40–50° for 2 days (562), gives (80% yield (561)) *N*,*N*-dimethylbenzylamine [Beil. XII-1019, XII_1-(448)], oil, fairly sol. cold but less sol hot aq., b.p. 183–184° cor. at 765.3 mm. (560), 180–181° at 749 mm. (540), 178–179° cor. (563), 177.8–178.2° cor. at 766 mm. (561), 178° u c. (562), 98–99° at 24 mm. (564), 83 5–85.5° at 21 mm. (565), 66–67° at 15 mm. (566), n_D^{20} = 1.5157 (564) (B̄.HCl, m.p. 175° (562) cf. (566); B̄.PkOH, m.p. 94° (532), 94–95° (559)).]

[C̄ with $(C_2H_5)_2NH$ in s.t. at 100° gives (567) (568) *N*,*N*-diethylbenzylamine [Beil. XII-1021, XII_1-(448)], oil, spar. sol. aq., b.p. 212° (569), 211–212° (568) cor. (567), 209° (570) at 755 mm. (551), 96–98° at 17 mm. (564), 94° at 15 mm. (555) (B̄.PkOH, m.p. 120–121° (571), 119° (566)).]

With aromatic secondary amines. [C̄ htd. with *N*-methylaniline at 100° (521) (525) in pres. of aq. Na_2CO_3 (160), or C̄ with *N*,*N*-dimethylaniline + I_2 at 150° (504), or C̄ with mixt. of *N*-methylaniline and *N*,*N*-dimethylaniline at 150° (526), gives (yields: 92.5% (526), 60% (525), 41% (521)) *N*-benzyl-*N*-methylaniline (benzyl-methyl-phenylamine) [Beil. XII-1024, XII_1-(450)], b p. 305–306° (527), 187–188° at 26 mm. (525), 177–178° at 18 mm. (526), 171° at 13 mm. (528), 162–163° at 8 mm. (504); $D_{25}^{26.5}$ = 1.0421 (504), D_4^{15} = 1.0475 (528); $n_D^{29.5}$ = 1.6006 (504), 1.6071 (528). (B̄ PkOH, m p *131° (529), 128–128.5° (504),* 127° (525), 109° (530), 105–107° (531), 104° (532), 103.0–103 5° (533); note disagreement)]

[C̄ htd. with *N*-ethylaniline (534) in toluene + Na_2CO_3 (535), or C̄ with *N*,*N*-diethylan-

[C̄ with alc. K propionate (460) or with aq. Na propionate (160) gives benzyl propionate [Beil. VI-436, VI_1-(220), VI_2-(416)], b.p. 222°]

[C̄ with alc. K *n*-butyrate (460), or aq. Na *n*-butyrate (160), gives benzyl *n*-butyrate (1:3977).]

C̄ with salts of other aliphatic acids behaves similarly but detailed treatment will not be given here.

With salts of aromatic acids. [For extensive study of reaction of C̄ with NaOBz giving benzyl benzoate (1:4422) see (462) (629).]

With salts of enolic esters. [C̄ with diethyl sodiomalonate gives (yields: 87% (463), 85% (464), 60% (471), 51–57% (465), 50% (470)) (466) diethyl benzylmalonate [Beil. IX-868, IX_1-(381)], b.p. 300° (466), 296–298° (467), 195° at 22 mm. (463), 163° at 14 mm. (468), 170° at 13 mm. (469), 169° at 12 mm. (470) (471), 158° at 8 mm. (472), 128–133° at 6 mm. (473), 145–155° at 5 mm. (465), 150–152° at 4 mm. (474), 140–140.5° at 1.5 mm. (474), 105–108° at 1 mm (475) (476); D_4^{20} = 1.0750 (468); $n_D^{26.5}$ = 1.484 (475) (476), n_D^{20} = 1.4872 (468). This prod. on alk. hydrolysis (for study of kinetics see (477)) and subsequent acidification gives benzylmalonic acid [Beil IX-868, IX_1-(381)], cryst. from ether, C_6H_6, or $CHCl_3$/pet. ether, m.p. 120.6° (478), 120° (479), 120° dec. (468), 119–120° (480), 117–118° (472), 117° (466) (467); on htg. above its m.p. (480) this acid readily loses CO_2 yielding hydrocinnamic acid (1:0615), m.p. 48°.]

[C̄ with Na enolate of diethyl benzylmalonate (above) (482) (485), or C̄ with diethyl disodiomalonate (483), or C̄ with diethyl ethoxymagnesiomalonate (484), gives (yields: 85% (483), 84–87% (485)) diethyl dibenzylmalonate [Beil. IX-937, IX_1-(408)], b.p. 250° at 40 mm. (482), 256–257° at 38 mm. (486), 234–235° at 23 mm. (485), 224–226° at 15 mm. (484), 221° at 11 mm. (483), 192–193° at 2 mm. (487); m.p. 13–14° (486); D_4^{20} = 1.0930 (482). Note that this prod. always accompanies the diethyl benzylmalonate of preceding paragraph. Diethyl dibenzylmalonate with alc. alk. hydrolyzes with great difficulty (488) (485) but gives dibenzylmalonic acid [Beil IX-937, IX_1-(407)], m.p. 175° (485), 174° (488), which on htg. above its m.p. loses CO_2 giving dibenzylacetic acid (1:0668), m.p. 89°.]

[C̄ with ethyl sodioacetoacetate as directed (489) (490) (491), or C̄ with ethyl acetoacetate + BF_3 (492), gives (yields: 70% (491), 23% (492)) ethyl α-benzylacetoacetate [Beil. X-710], b.p. 283–284° u.c. (493), 276° (490), 157–158° at 14 mm. (494), 164–165° at 12 mm. (493), 163–165° at 12 mm. (491), 140–150° at 2–3 mm. (473) (corresp. 2,4-dinitrophenylhydrazone, m.p. 71.5° (473)). For ketonic cleavage of this prod. with 20% aq. NaOH (495) or aq in s.t. at 250° (496) giving benzylacetone [Beil. VII-314, VII_1-(167)], b.p. 236°, see indic. refs.]

[C̄ with ethyl acetoacetate as directed (497) cf. (501) or C̄ with ethyl α-benzylacetoacetate (above) as directed (489) (493) (498) (499) gives (58% yield (497)) ethyl α,α-dibenzylacetoacetate [Beil. IX-771], m.p. 57° (493) (497) (500), b.p. 230–234° at 12 mm. (493) cf. (497). For ketonic cleavage of this prod. with HI/AcOH giving (80% yield) α,α-dibenzylacetone, b.p. 190–192° at 15 mm., see (497); for acid cleavage giving dibenzylacetic acid (1:0668) see (500) (501).]

With amines. *With aliphatic primary amines.* [C̄ with [illegible]
in abs. EtOH gives (546) cf. (554) *N*-methylbenzylamine [illegible]
sol. aq., b.p. 184–186° (547) (554), 184–185° u.c. at 749 m[illegible]
(550), 180–181° cor at 765.5 mm. (546), 180° at 760 [illegible]
(B̄.HCl, 195° (554), 174–175° (546); B̄.PkOH, m.p. 117–118° (532), 113–116° (553)) Note that this prod. is usually accompanied by some *N*-methyl-dibenzylamine [Beil. XII-1036, XII_1-(453)], b.p. 304–305° cor. at 765.5 mm. (546), 165° at 15 mm (555), 161–162° at 12 mm. (556) (B̄.HCl, m.p. 200–201° (556); B̄.PkOH, m.p. 107° (557)), also obtd. from C̄ with *N*-methylbenzylamine (above) in pres. of NaOH at 145° for 4 hrs. (555).]

[illegible]
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iline + I_2 at 150° (504), or C̄ with a mixt of N-ethylaniline + N,N-diethylaniline at 150° (526), gives N-benzyl-N-ethylaniline (benzyl-ethyl-phenylamine) [Beil. XII-1026, XII_1-(450)], b p. 285–286° sl. dec. at 710 mm. (534), 212–220° at 54 mm. (526), 185 5–186 5° at 22 mm. (535) (536), 173° at 12 mm. (528), 163–164° at 6 mm. (504); D_4^{15} = 1.0330 (528); n_D^{15} = 1 5975 (528) (B̄.PkOH, m.p 116–117° (536), 114° (535), 113–114° (504), 111–112° (533)). — For important study of sulfonation of N-benzyl-N-ethylaniline see (537).]

With heterocyclic secondary amines. [C̄ with piperidine reacts vigorously giving (538) (541) (542) N-benzylpiperidine [Beil. XX-23, XX_1-(8)], b.p. 248° (539), 245–247° (540), 245° (538) (541), 119° at 13 mm (542); D_4^{20} = 0 96049 (542), D_4^{16} = 0.9625 (541), D_4^{15} = 0.96451 (542); n_α^{20} = 1 52269 (542) (B̄ HCl, m p. 178° (543)).]

[Direct reaction of C̄ with morpholine appears never to have been reported; the expected product, viz , N-benzylmorpholine [Beil XXVII-7, $XXVII_1$-(203)] (544), has, however, been prepd by many other methods and has following constants: b p. 260–261° cor. (545), 136–136 5° at 14 mm. (544), 128–129° at 13 mm. (542); D_4^{20} = 1.03874, D_4^{15} = 1.03396 (542) (B̄ HCl, m p. 244–245° dec (545), B̄ PkOH, m p 193 5–195° cor (544), 184–185° (545))]

With aliphatic tertiary amines. [C̄ with $(CH_3)_3N$ in abs. alc. (546) (561) (563) or abs. MeOH at 0° (572) gives trimethyl-benzyl-ammonium chloride [Beil. XII-1020, XII_1-(448)], m p 235° (572) dec (546); for studies of behavior of this prod toward cat. hydrogenation see (573) (574)]

[C̄ with $(C_2H_5)_3N$ directly (563) or at 100° in s.t (567) cf (570) gives triethyl-benzyl-ammonium chloride [Beil XII-1021], but its constants are not reported]

With aromatic tertiary amines [C̄ with N,N-dimethylaniline at ord. temp. (575) (577) in MeOH or EtOH (576) gives dimethyl-phenyl-benzyl-ammonium chloride [Beil. XII-1025, XII_1-(450)], tbls of monohydrate from aq. or alc , m p 110° (575), 109.5° (578), m.p. anhydrous form, 116° (577); for studies of rate of formn. of this salt in MeOH at 29° and 38° see (579), for studies of behavior on cat hydrogenation see (573) (580); for use of this quaternary salt as reagt. for introduction of benzyl radical see (473)]

[C̄ with N,N-diethylaniline in dry C_6H_6 refluxed 30 min gives (581) diethyl-phenyl-benzyl-ammonium chloride, m p 104° (581)]

With heterocyclic tertiary amines. [C̄ with pyridine directly (582) (583) (584) (585) (586) or on htg at 150° for 6 hrs. (587) gives N-benzylpyridinium chloride [Beil XX-218, XX_1-(74)], but this salt is difficult to crystallize (586) and its properties are not well established; for kinetics of the addition see (4) (579) — Note that C̄ with pyridine in pres. of Cu on htg gives (588) a mixt. of 2-benzylpyridine and 4-benzylpyridine, but this type of nuclear benzylation cannot be discussed here]

With arylhydrazines. C̄ (1 mole) with phenylhydrazine (2 moles) mixed with cooling (589) and subsequently htd at 115–120° (590) (591) (592), or refluxed in alc. (593), or C̄ with phenylhydrazine + Na in C_6H_6 (594) or liq. NH_3 (595), or C̄ with phenylhydrazine + $NaNH_2$ in liq NH_3 (73% yield (595)), gives N-benzyl-N-phenylhydrazine (α-benzyl-phenylhydrazine) [Beil XV-532, XV_1-(164)], oil, b p. 216–218° at 38 mm (591), 207–208° at 10 mm. (593) (B̄ HCl, m p. 176–177° (596), 170° (593), 164–169° (595), 167° (594) (595), 166–167° (590); corresp. acetyl deriv., m.p. 121–122° (594) (595); corresp benzoyl deriv., m.p. 139–140° (590)); note that the N-benzyl-N-phenylhydrazine is often accompanied (593) (591) by some benzaldehyde N-benzyl-N-phenylhydrazone, m.p. 111–112° (590), 111° (593) (594). — The isomeric N-benzyl-N′-phenylhydrazine (β or *sym.*-benzyl-phenylhydrazine) [Beil XV-533, XV_1-(165)], m.p. 35–36°, is not obtd. by benzylation of phenylhydrazine but only by indirect methods.]

[For analogous use of C̄ in prepn of *asym*-benzyl-o-tolylhydrazine, *asym*-benzyl-m-tolylhydrazine, *asym*-benzyl-p-tolylhydrazine, etc , see (597)]

With arylhydroxylamines. [C̄ with N-phenylhydroxylamine in pyridine as directed

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Colorless crystals from alc. (2).

[For prepn. of C̄ (30–50% yield of mixed solid + liquid stereomers (2)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1% $AlCl_3$ for 5 days at 35–40° see (2); for formn. of C̄ from 1,2-dichloroethylene (3:5030) with HCl + $AlCl_3$ at 50° see (1).]

C̄ in CCl_4 treated with $AlCl_3$ remains colorless and the solution does *not* (2) evolve HCl, even on boilg.

C̄ in alc. treated with Zn dust gives (80% yield (2)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (2).

C̄ dissolved in hot alc. and titrated with $N/10$ KOH splits off 1.44–1.50 moles HCl (2).

[A pentachlorobutane obtained (3) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) + $AlCl_3$ may or may not be identical with C̄.]

3:0750 (1) Müller, Hönn, *J. prakt. Chem.* (2) **128**, 289–290 (1932). (2) Prins, *Rec. trav. chim.* **56**, 121–123 (1937). (3) Consortium für Elektrochem. Ind., Brit. 453,414, Oct. 8, 1936; *Cent.* **1937**, I 1012.

3:0765 p-CHLOROBENZALDEHYDE ClCHO C_7H_5OCl Beil. VII - 235
VII₁-(133)

M.P.	49°	(1)	B.P. 214.5–216.5°	at 760 mm.	(3)
	48°	(2) (3)	213–214°		(6) (8)
	47.5°	(4) (6)	213°	at 748 mm.	(9)
	47°	(5)	108–111°	at 25 mm.	(7)
	46–47°	(7)			

Colorless pl. with odor like benzaldehyde. — Volatile with steam. — Somewhat sol. cold aq., more sol. hot aq.; eas. sol. alc., ether, C_6H_6, CS_2, AcOH. — Forms spar. sol. $NaHSO_3$ cpd.

[For prepn. of C̄ from *p*-chlorotoluene (3:8287) with CrO_2Cl_2 (10), or by halogenation to *p*-chlorobenzal (di)chloride (3:6700) (7) (46) or *p*-chlorobenzal (di)bromide (11) and their subsequent hydrolysis with fumg. H_2SO_4 (6) (12) (13), conc. H_2SO_4 (7), anhydrous oxalic acid (8), or water in a s.t. at 170° (14) (15) see indicated refs.; from *p*-aminobenzaldehyde by diazotization and reactn. with CuCl (73% yield (16)) see (16) (17) (1); from *p*-chlorobenzyl chloride (3:0220) (or bromide) by boilg. with aq. $Pb(NO_3)_2$ in CO_2 (4) (5) or with hexamethylenetetramine (2); from *p*-chlorobromobenzene via *p*-chlorophenyl MgBr and its reactn. with ethyl orthoformate *(64% yield) (18)*; from *p-chlorobenzonitrile with* $SnCl_2$ (19); from chlorobenzene + HCN + $AlCl_3$ (20) or with CO + $AlCl_3$ (21); from *p*-chlorobenzylamine with hexamethylenetetramine (45) see indic. refs.]

C̄ with $KMnO_4$ (2) (4) (5) or even slowly in air oxidizes to *p*-chlorobenzoic ac. (3:4940), m.p. 236°. [For study of auto-oxidation see (22).] — C̄ on cat. hydrogenation (92% yield (23)) or electrolytic reductn. (24) or by actn. of iodo-magnesium hydrobenzoinate (84% yield (25)) gives *p*-chlorobenzyl alc., ndls. from C_6H_6/lgr., m.p. 71–72.5° (23). — C̄ with conc. alk. undergoes Cannizzaro reactn. (for study see (26) (28)) although presumable products, *p*-chlorobenzyl alc. and *p*-chlorobenzoic ac., have not been (by this reactn.) actually isolated. [For study of C̄ in mixed Cannizzaro reactn. see (27).]

C̄ on reduction with Ni/Al alloy (Raney Ni) in aq. alk. gives (60% yield (48)) toluene (1:7405).

C̄ with dil. KCN gives benzoin condensation yielding 4,4′-dichlorobenzoin, m.p. 85–87° (29), which on oxidn. with HNO_3 in AcOH yields 4,4′-dichlorodibenzil, m.p. 195–196° (29).

C̄ on htg. with NaOAc + Ac_2O for 8 hrs. at 180–200° undergoes Perkin reactn. giving (yield: 52% (13), 60% (17)) *p*-chlorocinnamic ac., m.p. 249–250° (17), 247° (13) (31). [This with Br_2 in $CHCl_3$ gives (30) *p*-chlorocinnamic acid dibromide, m.p. 191° (30).] — C̄ + malonic acid + pyridine gives alm. quant. yield (31) *p*-chlorocinnamic acid. [With-

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3:8538 ETHYL β-CHLOROCROTONATE $C_6H_9O_2Cl$ Beil. II - 416, II_1-(189), II_2-(396)

CH_3—C—Cl
‖
H—C—$COOC_2H_5$

B.P. [184° cor.	(1)]	D_4^{20} = 1.106 (3) (4)	n_D^{20} = 1.4587	(3)
179–180°	(2)	1.101 (7)		
77° at 15 mm.	(3)	$D_4^{19.2}$ = 1.1018 (7)	$n_D^{19.6}$ = 1.4588	(4)
76–77° at 14 mm.	(4) (5)			
75.3–76.0° at 14 mm.	(6)	$D_4^{17.9}$ = 1.1526 (6)	$n_D^{17.9}$ = 1.4509	(6)
66° at 10 mm.	(7)			

[*See also ethyl β-chloroisocrotonate* (3:8325).]

[For prepn. of C̄ from β-chlorocrotonic acid (3:2625) in EtOH with HCl gas (100% yield (2)) (4) or with conc. H_2SO_4 (7) see indic. refs.]

[For formn. of C̄ from ethyl acetoacetate (1:1710) with PCl_5 as a by-product of prepn. of ethyl β-chloroisocrotonate (3:8325) see (8) (9), but this is definitely not a good means of prepn. of C̄.]

[C̄ with Al/Hg in alc. on warming is both dehalogenated and hydrolyzed yielding (10) crotonic acid (1:0425); note that with C̄ this reactn. goes more readily than with the isomeric *ethyl β-chloro-isocrotonate* (3:8325).]

[C̄ (2 moles) with K_2S (1½ moles) in 5 vols. abs. EtOH refluxed 16 hrs. (11) or C̄ with Na enolate of ethyl thioacetoacetate (14) gives (53% yield (11)) diethyl β,β′-thiodicrotonate

$S(—C(CH_3)=CH.COOC_2H_5)_2$, b p. 150–153° at 4 mm. (11), accompanied by some ethyl β-mercaptocrotonate (see below).]

[C̄ with alc. NaSH (12) or alc. KSH (11) (13) gives (30% yield (13)) ethyl β-mercaptocrotonate; note that this prod. is apparently a mixt. of the two geom. stereoisomers of ethyl β-mercaptocrotonate with the corresp. keto form, viz., ethyl thioacetoacetate, $CH_3.CS\,CH_2\,COOC_2H_5$; for details see indic. refs — Note also that, since the same prod. results by similar treatment of the isomeric ethyl β-chloroisocrotonate (3:8325), a mixture of the stereoisomers can be used as the starting material.]

[C̄ with alkali derivs. of alcohols, phenols, mercaptans, etc., splits out alkali halide yielding corresp. ethyl β-substituted crotonates: e g., C̄ with Na allylate gives (9) ethyl β-allyloxycrotonate; C̄ with Na cinnamylate gives (9) ethyl β-cinnamyloxycrotonate; C̄ with Na phenolate gives (15) cf (16) ethyl β-phenoxycrotonate, b.p. 147–148° at 14 mm. (15); C̄ with Na salt of ethyl mercaptan gives (17) ethyl β-ethylmercaptoisocrotonate, b.p. 139–141° at 16 mm. (17); C̄ with Na salt of benzyl mercaptan gives (90% yield (17)) ethyl β-benzylmercaptocrotonate, cryst. from lgr., m.p. 64.5° (17). Note that in the first three of the five preceding examples either C̄ or the isomeric ethyl β-chloroisocrotonate (3:8325) or their mixture gives the same result; for the last two, however, such is not the case.]

[C̄ with diethyl sodiomalonate gives (5) cf. (18) *trans* diethyl α-carbethoxy-β-methyl gluconate, $(C_2H_5OOC)_2CH.C(CH_3)=CH\,COOC_2H_5$ [Beil II-853], b p. 169–170° at 13 mm., $D_4^{20} = 1.0937$, $n_D^{20} = 1.4595$ (5); cf. behavior of stereoisomeric ethyl β-chloroisocrotonate (3.8325).]

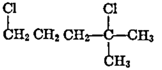
C̄ with phenylhydrazine gives the same (2) products as obtd. from the stereoisomeric ethyl β-chloroisocrotonate (3:8325): e.g., C̄ (1 mole) with phenylhydrazine (1 mole) at 100° for 6–8 hrs. gives by ring closure mainly (2) 3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-20, $XXIV_1$-(190)], pr. from aq., m.p. 127°, accompanied by small amts of 4-benzeneazo-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-*328*, $XXIV_1$-(319)], m p. 155–156°, and 3,3′-dimethyl-1,1′-diphenyl-*bis*-pyrazolone-5,5′ [Beil XXVI-484], dec. at high temp. without melting. — Note that with excess phenylhydrazine (2–4 moles) only traces of the 3-methyl-1-phenylpyrazolone-5 are formed while the amt. of the other two (less desirable) products is greatly increased (2).

3:8538 (1) Geuther, *Zeit. für Chemie* **1871**, 240. (2) Autenrieth, *Ber.* **29**, 1653–1664 (1896). (3) von Auwers, Wissenbach, *Ber.* **56**, 724 (1923). (4) von Auwers, *Ber.* **45**, 2807 (1912). (5) Gidvani, Kon, Wright, *J Chem Soc* **1932**, 1034–1035 (6) Errera, Lepingle, *Bull sci. acad.* [illegible] (7) von Auwers, *Ann* [illegible] 95). (9) Lauer, Kilburn, [illegible] *hem.* (2) **54**, 59–60 (1896). [illegible] izada, Schulze, *J. prakt.* [illegible] -474 (1931). (14) Mitra, [illegible] *Chem. Soc.* **79**, 1189–1190 [illegible], Voss, *Ber.* **53**, 385–388 (1920). (18) Fichter, Schwab, *Ann.* **348**, 251–256 (1906).

3:8540 ***d,l*-2,5-DICHLORO-2-METHYLPENTANE** $C_6H_{12}Cl_2$ **Beil. I - 148**

I_1—

I_2-(111)



B.P. 179–180° (1)

[For prepn. of C̄ from 5-chloro-2-methylpentanol-2 [Beil. I-410, I_2-(440)] with fumg. HCl or AcCl see (1); for formn. (together with other prods.) from dimethyl-cyclopropyl-carbinol [Beil. VI-10] by treatment with excess fumg. HCl see (2).]

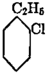
3:8540 (1) Henry, *Compt. rend.* **143**, 1224 (1906). (2) Bruylants, Dewael, *Bull. sci. acad. roy. Belg.* (5) **14**, 148 (1928); *Cent.* **1928**, I 2709; *C.A.* **22**, 3883 (1928).

3:8545 *n*-PROPYL β-CHLOROPROPIONATE $C_6H_{11}O_2Cl$ Beil. II-250
n-$C_3H_7O.CO.CH_2.CH_2Cl$ II_1—
II_2—

B.P. 179–181° (1) D_4^{20} = **1.0656** (2) n_D^{20} = **1.4290** (2)

3:8545 (1) Moureu, *Ann. chim.* (7) **2**, 172 (1894). (2) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

3:8550 *o*-CHLORO-ETHYLBENZENE C_8H_9Cl Beil. S.N. 467



B.P. 180° (1)

[For formn. of C̄ from ethylbenzene (1:7410) by chlorination (other products are also formed) see (1); for formn. from chlorobenzene (3:7903) with ethylene + $AlCl_3$ at 80° under pressure (3,5-diethyl-1-chlorobenzene is also formed) see (2).]

C̄ on oxidn. with alk. $KMnO_4$ yields (1) *o*-chlorobenzoic acid (3:4150).

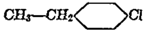
[C̄ on htg. with 15% NaOH + Cu powder for 2 hrs. at 315–320° in steel autoclave is thought (1) to undergo partial rearrangement, thus yielding some *m*-ethylphenol (1:1744).]

[C̄ on passing through an Fe or Ni-Cr tube at 675–700° is alleged (3) to lose HCl with production of phenylethylene (styrene) (1:7435).]

[C̄ on htg. with conc. NH_3 + CuO for 20 hrs. at 225° yields (2) *o*-aminoethylbenzene.]

3:8550 (1) Meharg, Allen, *J. Am. Chem. Soc.* **54**, 2920–2922 (1932). (2) Dreisbach (to Dow Chem. Co.), U.S. 2,159,370, May 23, 1939; *Cent.* **1939**, II 1775; *C.A.* **33**, 6875 (1939). (3) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct 16, 1928; *Cent.* **1929**, I 2922; *C.A.* **23**, 156 (1929).

3:8570 *p*-CHLORO-ETHYLBENZENE C_8H_9Cl Beil. V-354
V_1-(176)
V_2—



B.P. 180–182°	(1)	D_{20}^{20} = **1.0463** (4)	
180–181°	(2)		
179–180°	(3) (4)	D_4^{19} = **1.0575** (3)	
178–179° at 750 mm.	(5)		n_D^{18} = **1.5223** (3)
75–80° at 16 mm.	(5)		n_D^{16} = **1.5235** (4)

[*For prepn of C̄ from ethylbenzene (1:7410) with Cl_2 in the dark and in pres. of I_2* (2) or with SO_2Cl_2 + $AlCl_3$ (1) see indic. refs.; for prepn. of C̄ from chlorobenzene (3:7903) with EtBr + $AlCl_3$ (3) or EtOH + $AlCl_3$ (4) see indic. refs.; for prepn. of C̄ from *p*-chloroacetophenone (3:6735) by reduction with Zn/Hg + HCl (27% yield) see (5).]

C̄ on oxidn. with CrO_3 in AcOH (3) or with HNO_3 (2) yields *p*-chlorobenzoic acid (3:4940), m.p. 234° (3).

[C̄ on attempted nitration gives only (3) a liquid mixt. of isomers.]

[C̄ with Br_2 in AcOH + trace of I_2 yields (2) 3-bromo-4-chloro-ethylbenzene, b.p. 143–144° at 10 mm. (2); C̄ with Br_2 in $CHCl_3$ exposed in silica flask to sunlight yields (2) *p*-chloro-α-bromo-ethylbenzene, b.p. 120–121° at 8 mm. (2).]

[C̄ on htg. with 15% NaOH + Cu powder for 2 hrs. at 315–320° in a steel autoclave is thought (6) to undergo partial rearr., thus yielding *m*-ethylphenol (1:1744).]

[C̄ on passing through an Fe or Ni-Cr tube at 675–700° is alleged (7) to lose HCl with production of styrene (1.7435).]

3:8570 (1) Töhl, Eberhard, *Ber* **26**, 2944 (1893). (2) Varma, Sahay, Subrammonium, *J. Indian Chem. Soc.* **14**, 157–159 (1937). (3) Schreiner, *J. prakt. Chem.* (2) **81**, 557–558 (1910). (4) Tsukervanik, *J Gen. Chem* (*U.S.S.R.*) **8**, 1512–1515 (1938); *Cent.* **1939**, I 4929; *C.A.* **33**, 4587 (1939). (5) Lock, Bayer, *Ber* **72**, 1068 (1939). (6) Meharg, Allen, *J. Am. Chem Soc.* **54**, 2920–2922 (1932). (7) Smith (to Naugatuck Chem. Co), U.S. 1,687,903, Oct. 16, 1928; *Cent.* **1929**, I 2922; *C.A.* **23**, 156 (1929).

3:8575 1,5-DICHLOROPENTANE $C_5H_{10}Cl_2$ Beil. I - 131
(Pentamethylene dichloride) $Cl.CH_2.CH_2.CH_2.CH_2.CH_2.Cl$ I_1-(43)
I_2-(95)

B.P.			F.P.		
182.3° cor. at 760 mm.	(1)		**−72.8°** (1)	D_4^{25} = **1.0940** (3) (7)	
179.5–180.5°	(2)			**1.0918** (1)	
178–180°	(3)				
176–178° sl. dec.	(4)			D_4^{20} = **1.1028** (8)	n_D^{20} = **1.4563** (8)
102.4° at 60 mm.	(8)			**1.0697** (1)	
79–80° at 21 mm.	(4)				
76–78° at 21 mm.	(5)				
68° at 14 mm.	(4)				
64–66° at 10 mm.	(6)				

Colorless liq. with characteristic odor; sol. org. solv., insol aq.

[For prepn. (yield 77–78% (1); 75–80% (4)) from *N*-benzoylpiperidine [Beil. XX-46] + PCl_5 see (4) (1) (2); note that by-product benzonitrile may be removed by acid hydrolysis (4) (9) (2) or stdg with aq. (10); for prepn. from pentanediol-1,5 (1·6519) + PCl_5 in CCl_4 see (5); for prepn. from *N,N*-dibenzoylpentamethylenediamine + $SOCl_2$ see (11) (12); for forma. (19%) in direct chlorination of 1-chloropentane see (8).]

C̄ htd. in s.t. 5 hrs. at 130° with NaCN in MeOH yields (5) 1,5-dicyanopentane (pimelonitrile) which after hydrolysis with conc. HCl at 110° for 5 hrs. (5) gives pimelic acid (1:0456), m.p. 104° (5).

[For reaction with NaI in acetone see (8).]

Ⓓ **1,5-*bis*-**(Phthalimido)pentane [Beil. XXI-493]: from C̄ + K phthalimide in 60–70% yield (13) by htg. at 190–200°, pale yel. ndls from $CHCl_3$ + alc., m.p. 186° (13). [The half reaction prod., viz., 1-chloro-5-phthalimidopentane *N*-(ε-chloro-*n*-amyl)-phthalimide (14), has m.p 30–31° (14).]

—— Pentamethylene-ω,ω′-*bis*-(*isothiourea hydrochloride*): *monohydrate*, m.p. 206° (15), anhydrous cpd., m p. 210° (15). [From C̄ with thiourea (2 moles) in *n*-BuOH refluxed *1 hr.* (15).]

—— **1,5-Diphenoxypentane** (pentamethylene glycol diphenyl ether) [Beil. VI-147]: m.p 48–49° (16); b.p. 340° sl. dec., 215–217° at 12 mm. (16). [From C̄ in 75% yield on protracted boilg. (30 hrs.) with large excess (3 moles) sodium phenolate in alc. (16).]

3:8575 (1) Serwy, *Bull soc. chim Belg* **42**, 486, 488 (1933). (2) Clarke, *J. Chem Soc.* **101**, 1805 (1912) (3) Hilditch, Dunstan, *Z Elektrochem* **18**, 883 (1912). (4) von Braun, *Ber* **37**, 2918–2920 (1904). (5) Pummerer, Schönsamgruber, *Ber.* **72**, 1842 (1939). (6) Bost, Conn, *Oil Gas J.* **32**, No. 3, 17 (1933). (7) Dunstan, Hilditch, Thole, *J. Chem Soc.* **103**, 137 (1913). (8) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941) (9) von Braun, Sobecki, *Ber.* **44**, 1469 (1911). (10) Zappi, *Bull. soc. chim* (4) **19**, 249 (1916).

3:8595 *n*-BUTYL *d,l*-α-CHLOROPROPIONATE $C_7H_{13}O_2Cl$ Beil. S.N. 162

$$n\text{-}C_4H_9O.CO.\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}.CH_3$$

B.P. 183.5–185.0° at 760 mm. (1) $D_4^{20} = 1.0253$ (2) $n_D^{20} = 1.4263$ (2)
71.6–72.6° at 10 mm. (1)

3:8595 (1) Burkhard, Kahovec, *Monatsh.* **71**, 340 (1938). (2) Schjanberg, *Z. physik. Chem.* **A-172**, 230 (1935).

3:8596 ETHYL *d,l*-α-CHLORO-*n*-VALERATE $C_7H_{13}O_2Cl$ Beil. II-302
II₁—
II₂—

$$CH_3.CH_2.CH_2.\underset{\displaystyle Cl}{C}H.COOC_2H_5$$

B.P. 185° at 752 mm. (1) $D_-^{11.8} = 1.040$ (1) $n_-^{11} = 1.43071$ (1)

Liq. with peppermint-like odor; insol. aq.; sol. alc., ether.
[For prepn. of $\bar{C}$ from α-chloro-*n*-valeronitrile with abs. EtOH + HCl see (1).]

3:8596 (1) Servais, *Rec. trav. chim.* **20**, 47–48 (1901).

3:8597 ETHYL γ-CHLORO-*n*-BUTYRATE $C_6H_{11}O_2Cl$ Beil. II - 278
II_1-(124)
II_2-(254)

$$\underset{\displaystyle Cl}{C}H_2.CH_2.CH_2.COOC_2H_5$$

B.P. 186°	at 760 mm.	(1)	$D_4^{20} = 1.0754$ (4) $n_D^{20} = 1.43107$ (4)
183–184°		(2)	
77°	at 16 mm.	(3)	
76°	at 16 mm.	(4)	
72°	at 16 mm.	(12)	
70–71°	at 10 mm.	(5)	
64–66°	at 10 mm.	(6)	

[For prepn. of $\bar{C}$ from γ-chloro-*n*-butyric acid (3:0020) with EtOH + H_2SO_4 (80% yield (3)) see (3); from γ-chloro-*n*-butyronitrile with EtOH + HCl see (2); from γ-ethoxy-*n*-butyric acid by htg. with $SOCl_2$ (77% yield) see (5); from ethyl *n*-butyrate (1:3127) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (40% $\bar{C}$ + 10% α- and 40% β-isomers) see (7); from γ-ethoxy-*n*-butyryl chloride (12) in almost 100% yield merely by htg. at 100° for 10 hrs. see (12).]

$\bar{C}$ added dropwise to solid KOH at 180° loses HCl and by ring closure yields (8) ethyl cyclopropanecarboxylate [Beil. IX-4, IX_1-(3)], b.p. 134°.

[$\bar{C}$ heated with NaI in acetone yields (5) (6) (9) ethyl γ-iodo-*n*-butyrate, b.p. 69–71° at 3 mm. (5), 84–85° at 4 mm. (9); $\bar{C}$ with excess MeMgI yields (10) 5-chloro-2-methylpentanol-2; $\bar{C}$ with NaN_3 in aq alc. yields (11) ethyl γ-azido-*n*-butyrate; $\bar{C}$ with diethylamine in s.t. at 100° yields (3) ethyl γ-diethylamino-*n*-butyrate, b.p. 73–75° at 4 mm. (5).]

$\bar{C}$ on htg. with conc. HCl yields (5) γ-chloro-*n*-butyric acid (3:0020).

For the amide, anilide, *p*-toluidide, and other derivs. corresp. to $\bar{C}$ see γ-chloro-*n*-butyric acid (3:0020).

Ⓓ 1-Phenylpyrrolidone-2 [Beil. XXI-237]: cryst. from aq., m.p. 69° (12). [From $\bar{C}$ with aniline at 110° for 1 hr. (12).]

3:8597 (1) Henry, *Bull. acad. roy. Belg.* (3) **35**, 507–520 (1898); *Cent.* **1898**, II 273 (2) Henry, *Bull. soc. chim.* (2) **45**, 341 (1886). (3) Wohlgemuth, *Ann. chim.* (9) **2**, 307, 316 (1914). (4) Karvonen, *Ann. Acad. Sci. Fennicae* **A-10**, No. 4, p. 21; *Cent.* **1919**, III 808. (5) Blicke, Wright, Zienty, *J. Am. Chem. Soc.* **63**, 2489–2490 (1941) (6) Conant, Kirner, *J. Am Chem. Soc.* **46**, 249 (1924). (7) Price, Schwarcz, *J. Am. Chem. Soc.* **62**, 2894–2895 (1940). (8) Rambaud, *Bull. soc. chim.* (5) **5**, 1564 (1938). (9) Fuson, Arnold, Cooke, *J. Am. Chem. Soc.* **60**, 2272 (1938) (10) Henry, *Compt. rend.* **143**, 1223 (1906).

(11) Curtius, Giulini, *Ber.* **45**, 1046 (1912). (12) Prelog, Heimbach-Juhasz, *Ber.* **74**, 1703–1704 (1941).

3:8600 2-CHLORO-1,4-DIMETHYLBENZENE (*eso*-Chloro-*p*-xylene)

C_8H_9Cl Beil. V - 384, V_1-(186), V_2—

B.P. 186.8°	(1)	M.P. +2° (2)		D_4^{15} = 1.0589 (4)
186° at 767 mm.	(2)	+1.6° (4)		
183.6–185.6°	(3)			
181°	(4)			
183–184°	(5)			

[For prepn. of C̄ from *p*-xylene (1:7415) with Cl_2 in pres. of Fe (82–86% yield (4)) (5) or I_2 (2), by refluxing with $PbCl_4.2NH_4Cl$ (6), with $SO_2Cl_2 + AlCl_3$ (7), or with Cl_2 aq. (1) see indic. refs.; for prepn. of C̄ from *p*-xylidine [Beil. XII-1135, XII_1-(488)] via diazotization and use of Cu_2Cl_2 reaction see (3).]

C̄ on nitration with a mixt. of $HNO_3 + H_2SO_4$ acids as directed (4) (8) gives 5-nitro-2-chloro-1,4-dimethylbenzene, cryst from ether, m p. 77–78° (4), 78° (8) (*accompanied by other products*). [This mononitro-C̄ on further nitration yields 5,6-dinitro-2-chloro-1,4-dimethylbenzene, cryst. from alc., m p. 101° (4).]

C̄ on monosulfonation with fumg H_2SO_4 (2), 100% H_2SO_4 (4), or chlorosulfonic acid (9) yields 2-chloro-1,4-dimethylbenzenesulfonic acid-5 [Beil. XI-127] (corresp. sulfonyl chloride, m.p. 50° (4) (9); sulfonamide, m.p. 185° (4); sulfonanilide, m.p. 155° (4)).

[C̄ on further chlorination yields mainly 2,5-dichloro-1,4-dimethylbenzene [Beil. V-384], m.p. 71° (2) (4), b.p 221° cor. (2), 224° at 770 mm (4) (together with small amts. of other prods.).] [*For side-chain chlorination of C̄ and conversion of resultant prods. by hydrolysis to 2-chlorobenzenedicarboxylic acid-1,4* (chloroterephthalic acid) (3 4995) *see* (10).]

C̄ with Br_2 + Fe (5) or with $Br_2 + HNO_3 + H_2SO_4$ (11) as directed yields 5-bromo-2-chloro-1,4-dimethylbenzene [Beil. V-385], lfts. from hot alc., m p. 66° (5) (11). [Some dibromo-C̄, m.p. 93°, and tribromo-C̄, m.p. 234°, are also formed (5).]

3:8600 (1) Datta, Fernandes, *J Am. Chem. Soc.* **38**, 1811 (1916) (2) Kluge, *Ber.* **18**, 2099 (1885). (3) Kohlrausch, Pongratz, *Monatsh.* **64**, 369 (1934) (4) Wahl, *Ann. chim* (11) **5**, 5–82 (1936) (5) Willgerodt, Wolfien, *J. prakt. Chem.* (2) **39**, 402–405 (1889) (6) Seyewetz, Biot, *Compt. rend* **135**, 1121 (1902). (7) Töhl, Eberhard, *Ber* **26**, 2942 (1893). (8) Varma, Raman, *J Indian Chem Soc.* **12**, 540–541 (1935). (9) I.G., Brit. 281,290, Jan. 25, 1928; French 641,319, Oct. 5, 1928; *Cent* **1929**, II 352. (10) I.G., French 663,791, Aug. 26, 1929; *Cent.* **1929**, II 2731

(11) Varma, Raman, *J. Indian Chem. Soc.* **12**, 245 (1935).

C̄ on oxidn. with dil. HNO_3 in a s.t. yields (2) (3) 3-chloro-2-methylbenzoic acid (3:4435).

[The behavior of C̄ on nitration has not as yet been reported, all three possible mononitro derivatives have, however, been independently prepared; viz., 4-nitro-C̄, m.p. 46° (4); 5-nitro-C̄, m.p. 101° (5); 6-nitro-C̄, m.p. 62° (6).]

C̄ on sulfonation yields exclusively 3-chloro-1,2-dimethylbenzenesulfonic acid-6 [Beil. XI-121] (corresp. sulfonyl chloride as yet unreported; corresp. sulfonamide, m.p. 199° (2)).

[C̄ with Cl_2 in pres. of Fe yields (1) 3,4-dichloro-1,2-dimethylbenzene, b.p. 234°, m.p. 8–9° (2).]

3:8645 (1) Hinkel, Ayling, Walters, *J. Chem. Soc.* **1934**, 1947–1948. (2) Krüger, *Ber.* **18**, 1755–1758 (1885). (3) Claus, Bayer, *Ann.* **274**, 305–311 (1893). (4) Hinkel, Ayling, Walters, *J. Chem. Soc.* **1934**, 287. (5) Hinkel, *J. Chem. Soc.* **125**, 1852–1853 (1924). (6) Hinkel, Collins, Ayling, *J. Chem. Soc.* **123**, 2972 (1923).

3:8650 1,1-DICHLOROHEPTANE

$C_7H_{14}Cl_2$ Beil. I - 154, I_1-(57), I_2-(117)

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2—\overset{Cl}{\underset{Cl}{CH}}$$

B.P. 191° cor. (1)
82–84° at 30 mm. (2)
82° at 20 mm. (3)

D_4^{20} = **1.011** (3) n_D^{20} = **1.4440** (3)

[For prepn. of C̄ from *n*-heptaldehyde (1:0183) with PCl_5 at 150° (1) (2) (16% yield (6)), in the cold (61% yield (4)) (11), or in C_6H_6 at 20° (3) (50% yield (5)), see indic. refs. (much loss is incurred by polymerization of the initial aldehyde by the HCl resulting in the reactn.).]

C̄ with alc. KOH gives (1) (2) 1-chloroheptene-1 (3:8219) and on protracted actn. (1) (2) heptyne-1 (1:8085), b.p. 100°. — C̄ passed over soda-lime at 420° (3) (5) or htd. with powdered KOH + mineral oil at 250° (5) or dropped onto $NaNH.C_6H_5$ (7) or treated with $NaNH_2$ in xylene or mineral oil (60% yield (8) (10)) (9) gives *n*-amylacetylene (heptyne-1) (1:8085).

[For conversion of C̄ to 1,1-difluoroheptane by use of HgO + HF see (6).]

3:8650 (1) Limpricht, *Ann.* **103**, 81–82 (1857). (2) Welt, *Ber.* **30**, 1496 (1897). (3) Bachmann, Hill, *J. Am. Chem. Soc.* **56**, 2730–2732 (1934). (4) Loevenich, Losen, Dierichs, *Ber.* **60**, 951 (1927). (5) Hill, Tyson, *J. Am. Chem. Soc.* **50**, 172–176 (1928). (6) Henne, Renoll, Leicester, *J. Am. Chem. Soc.* **61**, 938–940 (1939). (7) Bodroux, *Compt. rend.* **208**, 1023 (1939). (8) Bourgeul, *Ann. chim.* (10) **3**, 223–224 (1925). (9) Meunier, Desparmet, *Bull. soc. chim.* (4) **35**, 481–482 (1924). (10) Guest, *J. Am. Chem. Soc.* **47**, 862 (1925).
(11) Kuz'min, *Soobschemie o Nauch.-Isslodovatel Rabote Kiev Ind. Inst.* **2**, 18 (1940); *C.A.* **37**, 3047 (1943).

3:8655 ISOBUTYL β-CHLOROPROPIONATE

$C_7H_{13}O_2Cl$ Beil. II-250, II_1—, II_2—

$(CH_3)_2CH.CH_2.O.CO.CH_2.CH_2Cl$

B.P. 191–193° (1) D_4^{20} = **1.0323** (2) n_D^{20} = **1.4295** (2)

3:8655 (1) Moureu, *Ann. chim.* (7) **2**, 172–173 (1894). (2) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

out, pyridine reactn. gives (100% yield (31)) *p*-chlorobenzalmalonic acid, m.p. 197–198° dec. (31).]

C̄ on mononitration with conc. HNO_3 + conc. H_2SO_4 at 80–90° gives (32) (33) 4-chloro-3-nitrobenzaldehyde [Beil. VII-262], ndls. from $CHCl_3$/lgr. or from aq , m p. 62° (32) (33); ndls. from dil. alc., m.p. 64.5° (34) [oxime, pale yel. ndls. from alc., m.p. 146° (34), 141.5–142.5° (35); phenylhydrazone, m p. 148.5–149 5° (35), *p*-nitrophenylhydrazone, or. ndls., m.p. 278–279° (34); semicarbazone, yel. ndls., m.p 244–245° dec. (35)].

C̄ htd. at 100° with 1 mole aniline gives (16) (36) *p*-chlorobenzalaniline, pale yel. pl., from alc., m.p. 62° (16) (36); C̄ htd. with 1 mole *p*-toluidine gives (16) (36) *p*-chlorobenzal-*p*-toluidine, colorless ndls from alc., m p. 125° (16) (36).

[For conversion of C̄ with MeMgX to *p*-chlorophenyl-methyl-carbinol and dehydration of latter to *p*-chlorostyrene see (46).]

- Ⓓ ***p*-Chlorobenzaldoxime** (*anti* form): cryst. from alc., m p. 106–107° (6) (37). [From C̄ + $NH_2OH.HCl$ + Na_2CO_3 (6); the *syn* isomer has m.p. 142° (37), 140° (6), and on fusion is converted to *anti* isomer (6).]
- Ⓓ ***p*-Chlorobenzaldehyde phenylhydrazone:** lt. yel. cryst. from dil. alc., m.p. 127–127.5° (35), 126–128° (38). [For study of kinetics of formn. see (39).]
- Ⓓ ***p*-Chlorobenzaldehyde *p*-nitrophenylhydrazone:** dk. br. cryst. from alc., m.p. 216.5° u.c. (40), 224° (41), 218–220° (35).
- Ⓓ ***p*-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone:** or. cryst., m.p. 270° (42), 265° (45), 264° cor. (43). [Use in detn. of C̄ (43).]
- Ⓓ ***p*-Chlorobenzaldehyde semicarbazone:** tbls. from pyridine (10), ndls. from MeOH (44, m.p. 230° (10) (47), 232–233° (44).

3:0765 (1) Blanksma, *Chem. Weekblad* **6**, 909 (1909). (2) Mayer, English, *Ann.* **417**, 78–79 (1918). (3) Kahovec, Kohlrausch, *Z. physik. Chem.* **B-38**, 138 (1937). (4) Jackson, White, *Ber.* **11**, 1043 (1887). (5) Jackson, White, *Am. Chem. J.* **3**, 31–32 (1881). (6) Erdmann, Schwechten, *Ann* **260**, 63–65 (1890). (7) McEwen, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 133–135 (1943). (8) Erdmann, Kirchhoff, *Ann.* **247**, 368 (1888). (9) Hoechster Farbwerke, Ger. 207,157; *Cent* **1909**, I 962. (10) Law, Perkin, *J. Chem. Soc.* **93**, 1636 (1908).

(11) Lock, Bayer, *Ber.* **72**, 1067 (1939). (12) Kaeswurm, *Ber.* **19**, 742 (1886). (13) Böck, Lock, Schmidt, *Monatsh.* **64**, 407 (1934) (14) Beilstein, Kuhlberg, *Ann.* **146**, 328 (1868). (15) Beilstein, Kuhlberg, *Ann* **147**, 352–353 (1868). (16) von Walther, Raetze, *J. prakt. Chem.* (2) **65**, 259–264 (1902). (17) van der Lee, *Rec trav. chim.* **45**, 678–680 (1926) (18) Bodroux, *Compt. rend.* **138**, 701 (1904); *Bull. soc. chim* (3) **31**, 585–588 (1904). (19) Stephen, *J. Chem. Soc.* **127**, 1874 (1925). (20) Hinkel, Ayling, Benyon, *J. Chem. Soc* **1936**, 342.

(21) Ger. 281,212, Dec. 15, 1914, *Cent.* **1915**, I 178; Ger. 403,489, Sept. 29, 1924; *Cent.* **1925**, I 1369; Brit. 334,009, Sept. 18, 1930; *Cent.* **1930**, II 3850. (22) van der Beek, *Rec. trav. chim.* **51**, 411–413 (1932). (23) Carothers, Adams, *J. Am. Chem. Soc* **46**, 1681–1682 (1924). (24) Law, *J. Chem. Soc.* **99**, 1114–1115 (1911). (25) Shankland, Gomberg, *J. Am. Chem. Soc.* **52**, 4975 (1930). (26) Eitel, Lock, *Monatsh.* **72**, 392–409 (1939). (27) Bailar, Barney, Miller, *J. Am. Chem. Soc.* **58**, 2110–2111 (1936). (28) Molt, *Rec. trav chim.* **56**, 233–246 (1937). (29) Gomberg, Van Natta, *J. Am. Chem. Soc.* **51**, 2241 (1929). (30) Wilstaedt, *Ber* **64**, 2693 (1931).

(31) K. C. Pandya, R. B. Pandya, *Proc. Indian Acad. Sci.* **14-A**, 112–122 (1941); *C.A.* **36**, 1599 (1942). (32) Erdmann, Ernst, Hugho, *Ann.* **294**, 380 (1897). (33) Hodgdon, Smith, *J. Soc. Chem. Ind.* **49**, T408–410 (1930). (34) Hodgson, Beard, *J. Chem. Soc.* **1927**, 20. (35) van der Lee, *Rec. trav. chim.* **45**, 278–281 (1926). (36) DeGaouck, LeFevre, *J. Chem Soc.* **1938**, 741–742. (37) Brady, McHugh, *J. Chem. Soc.* **125**, 551 (1924). (38) Charlton, Earl, Kenner, Luciano, *J. Chem. Soc.* **1932**, 40. (39) Bodforss, *Z. physik. Chem.* **109**, 242 (1924). (40) Shoppee, *J. Chem. Soc.* **1931**, 1232.

(41) Hodgson, Handley, *J. Chem. Soc.* **1928**, 1886. (42) Blanksma, Wackers, *Rec. trav. chim.* **55**, 658 (1936). (43) Eitel, Lock, *Monatsh.* **72**, 389–390 (1939). (44) Henderson, Heilbron, [illegible]

J. Org. Chem. **9**, 1–8 (1944).

(8) Rambaud, *Bull. soc. chim.* (5) **5**, 1552–1565 (1938). (9) Rambaud, *Compt. rend.* **200**, 2089–2091 (1935). (10) Rambaud, *Bull. soc. chim.* (5) **1**, 1347 (1934).
(11) Rambaud, *Bull. soc. chim.* (5) **1**, 1328 (1934).

3:8660 *p*-XYLYL CHLORIDE (*p*-Methylbenzyl chloride; ω-chloro-*p*-xylene)

C_8H_9Cl Beil. V - 384
V_1-(186)
V_2-(299)

B.P. 192°	at 760 mm.	(1)
98–101°	at 27 mm.	(2)
92–94°	at 20 mm.	(1)
90°	at 20 mm.	(3)
81.5°	at 15 mm.	(4)

$D_4^{20} = 1.0512$ (2) $n_D^{-} = 1.5380$ (2)

[For prepn. of C̄ from *p*-tolylcarbinol (1:5954) by distn. with HCl see (3) (4A) (8); by treatment with PCl_3 (87% yield) see (6); for prepn. from toluene (1:7405) with paraformaldehyde + HCl (75% yield (2)) see also (5); with *sym.*-dichlorodimethyl ether (3:5245) + $ZnCl_2$ see (1) (5).]

C̄ stood with $N/10$ alc. NaOEt at 30° yields ethyl *p*-xylyl ether [Beil. VI-498], b.p. 203°, to extent of 15% yield in 6 hrs., 40.5% in 24 hrs. (7) cf. (8) (9). [For data on rate of hydrolysis with acid or alk. in acetone soln. at 30° see (10).]

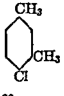
C̄ with Mg in ether yields RMgCl; on carbonation at 0° (11) this yields *p*-$CH_3.C_6H_4.CH_2.COOMgCl$; this upon acidification presumably (no record) would yield *p*-tolylacetic ac. [Beil. IX-530], m.p. 92°; on treatment (12) with C_2H_5MgBr, however, it gives a mixt. contg. *64.2% p*-tolylmalonic ac., sepd. with C_6H_6, cryst. from aq., m.p. *143.5–144.5°* with evoln. of CO_2 (12). [Use of isopropyl MgCl instead of C_2H_5MgBr gave 93% *p*-tolylmalonic ac. (12).]

C̄ boiled for 6 hrs. with 10 pts. 7% $NaHCO_3$ soln. gave (66% yield (2)) *p*-tolylcarbinol (1:5954).

Ⓓ *N*-(*p*-Xylyl)phthalimide [Beil. XXI-468]: from C̄ by htg. at 180° with K phthalimide (3); ndls. (from dil. alc.), m.p. 116–117° (3), 120° (13).

3:8660 (1) Stephen, Short, Gladding, *J. Chem. Soc.* **117**, 520 (1920). (2) Shorygin, Bogdanowa, *J. Applied Chem. (U.S.S.R.)* **11**, 1217–1221 (1938); *Cent.* **1939**, II 1277; *C.A.* **33**, 4216 (1939). (3) [illegible] *J. prakt. Chem.* (2) **62**, 111 (1900). (4) Bennett, Jones, *J. Chem. Soc.*
41). (5) Hill, Short, *J. Chem.*
. (7) Franzen, *J. prakt. Chem.*
. (9) von Braun, Engel, *Ann.*
(1934).
Ivanoff, Pchenitchny, *Bull. soc.*
78 (1922).

3:8665 4-CHLORO-1,3-DIMETHYLBENZENE (*unsym.*-Chloro-*m*-xylene)



C_8H_9Cl Beil. V - 373
V_1-(183)
V_2-(291)

B.P. 192.2–193.9°		(1) (?)
187–188°	at 755 mm.	(2)
186.5° cor.	at 767 mm.	(3)
183–184°		(6)
73–75°	at 16 mm.	(4)

$D_{20}^{20} = 1.0598$ (3) $n_D^{25} = 1.5230$ (5)

3:8657 ETHYL γ-CHLOROCROTONATE $C_6H_9O_2Cl$ Beil. II - 418
II_1—
II_2-(397)

$CH_2.CH{=}CH.COOC_2H_5$
|
Cl

B.P. 191–193°	at 760 mm. (1)	$D_4^{15} = 1.130$ (2)	$n_D^{15} = 1.4625$ (2)
84–85°	at 15 mm. (2)		
80°	at 10 mm. (3)		
77–82°	at 12 mm. (4)		
66–68°	at 2 mm. (3)		

[*See also γ-chlorocrotonic acid* (3:2170).]

Although C̄ is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that C̄ is the *trans* stereoisomer.

[For prepn. of C̄ from ethyl vinylacetate [Beil. II-407] (5) with Cl_2 in CCl_4 (forming ethyl β,γ-dichloro-*n*-butyrate) followed by treatment with alc. NaOEt at 0° (splitting out HCl) and giving 65% yield see (5); from ethyl γ-chloro-β-hydroxy-*n*-butyrate [Beil. III-310, III_1-(116)] by dehydration with P_2O_5 (yields: 65% (4), 62.5% (3), 60% (2)) (6) (accompanied by some γ-chlorocrotonic acid (3:2170) (3) (2) and also by ethyl γ-chlorovinylacetate (3)) see indic. refs.]

C̄ on hydrolysis with $Ba(OH)_2$ below 0° or even (but less advantageously) with KOH gives (60% yield (3) (5)) (7) (2) γ-chlorocrotonic acid (3:2170), m.p. 83°; note, however, that hydrolysis with hot conc. alk. gives also two other products, viz., $O(CH_2{-}CH{=}CH.COOH)_2$, m.p. 195° (2), and γ-hydroxycrotonic acid, m.p. 108° (2).

[C̄ *in EtOH/NaOEt* undergoes *addition* of EtOH to unsatd. linkage followed to small extent by elimination of HCl with consequent ring closure to a cyclopropane deriv.; e.g., C̄ (0.134 mole) in 2½ pts. EtOH treated dropwise in cold with soln. of Na (0.087 mole) in the same vol. of EtOH as above gives (yields 42% (8), 25% (9)) ethyl γ-chloro-β-ethoxy-*n*-butyrate, b.p. 108.0–108.5° at 20 mm., $D_4^{17.5} = 1.078$, $n_D^{17.5} = 1.4295$ (8), accompanied by a little (3% yield (8)) ethyl 2-ethoxycyclopropane-1-carboxylate (1-carbethoxy-2-ethoxycyclopropane), b.p. 77.50–77.75° at 13 mm., $D_4^{13} = 0.995$, $n_D^{13} = 1.453$ (8); the latter is also obtd. (22% yield (8)) by distn. of the ethyl γ-chloro-β-ethoxy-*n*-butyrate with dry powdered KOH at 180° and 45 mm. press.]

[C̄ on dropwise addition to dry powdered KOH at 180° gives ethyl cyclopropane-1-carboxylate [Beil. IX-4, IX_1-(3)], b.p. 130° at 728 mm., $D = 0.970$, $n_D^{15} = 1.416$.]

[C̄ with excess dry powdered $CaBr_2$ heated several days under reflux gives (2) (10) ethyl γ-bromocrotonate. — C̄ (1 mole) with NaI (1 mole) in acetone reacts readily at ord. temp. pptg. NaCl (80% theory) and yielding (3) ethyl γ-iodocrotonate, b.p. 92–93° at 2 mm.]

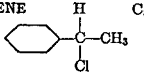
[C̄ with NaOAc in AcOH heated at 100° cf. (11) yields (8) ethyl γ-acetoxycrotonate, b.p. 115–116° at 15 mm., $D_4^{23} = 1.075$, $n_D^{23} = 1.4445$ (11).]

[C̄ with conc. aq. NH_4OH not only has its halogen replaced by $-NH_2$ but also is hydrolyzed with consequent formn. of γ-aminocrotonic acid; this was not isolatable as such but only as its picrate, the m.p. of which, however, is not reported (2).]

[C̄ with Me_3N (excess) in alc. contg. a trace of NaI in s.t. at 100° followed by evapn. with HCl gives (4) γ-dimethylaminocrotonic acid chloromethylate (γ-dimethylaminocrotonbetain chloride), m.p. 203–205° dec. (4).]

3:8657 (1) Lespieau, *Bull. soc. chim.* (3) **33**, 466–467 (1905). (2) Rambaud, *Bull. soc. chim.* (5) **3**, 139–141 (1936). (3) Braun, *J. Am. Chem. Soc* **52**, 3167–3176 (1930). (4) Linneweh, *Z. physiol. Chem.* **176**, 217–221 (1928). (5) Glattfeld, Rietz, *J. Am. Chem. Soc.* **62**, 976 (1940). (6) Lespieau, *Compt. rend* **130**, 1410 (1900). (7) Bacher, Benninga, *Rec. trav. chim.* **55**, 610 (1936).

3:8667 *d,l*-α-CHLOROETHYLBENZENE (Methyl-phenyl-carbinyl chloride) C_8H_9Cl Beil. V - 354 V_1-(177) V_2-(277)



B.P.	195° dec.	(1)	D_4^{20} = 1.0620 (9) n_D^{20} = 1.5276 (9)
	194° dec.	(2)	
	90–91° at 33 mm.	(3)	D_4^{13} = 1.0598 (6) n_D^{13} = 1.5337 (6)
	82–83° at 18 mm.	(4)	
	81–82° at 17 mm.	(5)	
	91–92° at 16 mm.	(6)	
	69–70° at 13 mm.	(7)	
	67.5° at 12 mm.	(8)	
	68° at 9 mm.	(9)	

$\bar{C}$ even on stdg. tends to lose HCl with formn. of styrene and styrene polymers (9); such decompn. is facilitated by pres. of any HCl and $\bar{C}$ could not be dried with P_2O_5 (10).

[Both opt. act. stereoisomerides of $\bar{C}$ are known but cannot be discussed here.]

[For prepn. of $\bar{C}$ from methyl-phenyl-carbinol (1:6475) with 6 *N* HCl (75% yield (3)) (7), with aq. HCl in pres. of $CaCl_2$ (2) (8), with HCl + $ZnCl_2$ (71% yield (11)), with $SOCl_2$ (82–88% yield (11)) (4) (5) (10), or with acetyl chloride (3:7065) (12) see indic. refs.; from ethylbenzene (1:7410) with Cl_2 in light (1) (13) (14) (15) or in pres. of 1% PCl_5 (90% yield (16)) see indic. refs.; from styrene (1:7435) by addn. of HCl (9) (17) (18) under press. in solvent (100% yield (19)) or at −80° (68% yield (29)) see indic. refs.; for formn. of $\bar{C}$ from methyl-phenyl-carbinyl MgBr during reaction with cyanogen chloride (47% $\bar{C}$ + 10% methyl-phenyl-carbinyl cyanide + 5% 2,3-diphenylbutane) see (6); for formn. of $\bar{C}$ from methyl phenyl ketone (acetophenone) (1:5515) during reduction with Zn/Hg + HCl see (20).]

[$\bar{C}$ passed at elevated temp. over dehydrohalogenating cat. (21), or htd. with pyridine in s.t. 6 hrs. at 130° (77% yield (22)), or boiled with a small excess quinoline for ½ hr. (75–80% yield (16)) (23), or its quat. salt with pyridine htd. in vac. (24), or htd. with acids less volatile than HCl (25), or htd. with salts of org. bases (26) (23) yields styrene (1:7435), b.p. 145°.]

[$\bar{C}$ with H_2 and Pd in pres. of MgO as specified (8) gives rapidly and quant. ethylbenzene (1:7410); note that $\bar{C}$ reduces much more readily than the isomeric β-chloroethylbenzene (3:8712) (8).]

$\bar{C}$ on hydrolysis, e.g., by boilg. with 25% excess of 10–15% aq. Na_2CO_3 soln., gives (90% yield (16)) (27) methyl-phenyl-carbinol (1:6475) q.v.; $\bar{C}$ with aq. alc. or with aq. alc. NaOH gives at 50° only (5) methyl-phenyl-carbinol; at 100° both styrene (1:7435) and α,α-diphenyl-diethyl ether are also formed (5); under certain circumstances α-diphenyl-diethyl ether may also appear (5) (1). [For study of hydrolysis of $\bar{C}$ in acetone contg. $HgCl_2$ see (4).]

[$\bar{C}$ with aq. Na_2SO_3 on boilg. for 9 hrs. (14) (7) gives (43–45% yield (14)) sodium α-phenylethanesulfonate (corresp. sulfonyl chloride, ndls. from alc., m.p. 79° (14) cf. (7), corresp. sulfonamide and anilide are unreported).]

$\bar{C}$ on oxidn. with $Cu(NO_3)_2$ (13) or on boilg. with aq. or dil. alc. soln. of hexamethylenetetramine (28) gives (60% yield (13)) methyl phenyl ketone (acetophenone) (1:5515).

3:8667 (1) Schramm, *Monatsh.* **8**, 101–105 (1887). (2) Engler, Bethge, *Ber.* **7**, 1127 (1874). (3) Norris, Watt, Thomas, *J. Am. Chem. Soc.* **38**, 1078 (1916). (4) Read, Taylor, *J. Chem. Soc.* **1940**, 681. (5) Ward, *J. Chem. Soc.* **1927**, 445–458. (6) Grignard, Ono, *Bull. soc. chim.* (4)

[For prepn. of C̄ from 1,2-dimethylbenzene (*m*-xylene) (1:7420) with Cl_2 in pres. of I_2 see (6) (3), with SO_2Cl_2 in the dark see (7), as by-product in prepn. of *m*-xylyl (di)chloride (3:8700) see (5); for prepn. of C̄ from 4-amino-1,2-dimethylbenzene (*unsym.-m*-xylidine) [Beil. XII-1111, XII_1-(483)] via diazotization and use of Cu_2Cl_2 reaction see (2) (1); for formn. of C̄ from 1,3-dimethylbenzenesulfonic acid-4 [Beil. XI-123, XI_1-(34)] by htg. with $SOCl_2$ in a s.t. at 160° for 3–4 hrs. see (8); for formn. of C̄ from 4-bromo-1,3-dimethylbenzene via conversion to RMgBr and reactn. with Cl.CN see (4); for prepn. of C̄ from *p*-chlorotoluene (3:8287) by chloromethylation with CH_2O + HCl to 4-chloro-3-(chloromethyl)-toluene and subsequent reduction with Zn + NaOH see (20)]

[For reactn. of C̄ with 4,4′-tetramethyldiaminobenzophenone (Michler's ketone) + Na in toluene yielding *bis*-(4-dimethylaminophenyl)-4-*m*-xylylcarbinol, odorless ndls. from m.p. 145°, see (9); for use of this prod. in prepn. of homologs of malachite green alc., (10) (11) and other dyestuffs (12) see indic. refs.]

C̄ on oxidn. with $K_2Cr_2O_7$ + H_2SO_4 (6) (3) (7) yields 4-chloro-3-methylbenzoic acid (3.4915), cryst. from aq., m.p. 209–210° (3) (7). — C̄ on oxidn. with aq. $KMnO_4$ gives (13) (14) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4980), ndls. from hot aq , m.p. 294.5° (14), 295° (13).

C̄ in Ac_2O treated with mixt. of HNO_3 + H_2SO_4 as specified (15) yields 6-nitro-4-chloro-1,3-dimethylbenzene [Beil. V-379, V_1-(184)], m.p. 42° (15). [The other mononitro derivs. of C̄ have been prepd. indirectly, viz., 5-nitro-C̄ [Beil. V-379] (16), m.p. 51°; 3-nitro-C̄, m.p. 72–73° (17).]

C̄ on sulfonation with a mixt. of equal pts fumg. H_2SO_4 + conc. H_2SO_4 yields (18) 4-chloro-1,3-dimethylbenzenesulfonic acid-6 [Beil. XI-123] (corresp. sulfonamide, m.p. 195° (3)).

C̄ on bromination with Br_2 + HNO_3/H_2SO_4 mixt. (19) yields 6-bromo-4-chloro-1,3-dimethylbenzene [Beil. V-374], m.p. 66° (19).

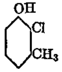
3:8665 (1) Kohlrausch, Pongratz, *Monatsh.* **64**, 370 (1934). (2) Klages, *Ber.* **29**, 310 (1896). (3) Jacobsen, *Ber.* **18**, 1761 (1885). (4) Grignard, Bellet, Courtot, *Ann. chim.* (9) **4**, 45 (1915). [illegible]

I 1274.

[illegible]

chim. (2) **28**, 343 (1877). (19) Varma, Raman, *J. Indian Chem. Soc* **12**, 248 (1935). (20) Tschunkur, Eichler (to I.G.), Ger. 509,149, Oct. 8, 1930; *Cent.* **1931**, I 360; [*C.A.* **25**, 711 (1931)].

—— **2-CHLORO-3-METHYLPHENOL** C_7H_7OCl Beil. VI — VI_1— VI_2-(355)



B.P. abt. **194°** **M.P. 55-56°**

See 3:1055. *Division A: Solids.*

$\bar{C}$ on sulfonation (4) (5) yields exclusively 4-chloro-1,2-dimethylbenzenesulfonic acid-5 [Beil. XI-121] (corresp. sulfonyl chloride, as yet unreported; sulfonamide, ndls. from alc., m.p. 207° (4)).

$\bar{C}$ with Cl_2 in pres. of Fe yields (2) 4,5-dichloro-1,2-dimethylbenzene, m.p. 76°, b.p. 240° (2).

3:8675 (1) Claus, Groneweg, *J. prakt. Chem.* (2) **43**, 257 (1891). (2) Hinkel, Ayling, Walters, *J. Chem. Soc.* **1934**, 1947–1948. (3) Kohlrausch, Pongratz, *Monatsh.* **64**, 371 (1934). (4) Krüger, *Ber.* **18**, 1756–1758 (1885). (5) Claus, Bayer, *Ann.* **274**, 305–309 (1893). (6) Huntress, Seikel, *J. Am. Chem. Soc.* **61**, 820 (1939). (7) Hinkel, Ayling, Walters, *J. Chem. Soc.* **1934**, 286–287.

3:8680 *n*-OCTANOYL CHLORIDE (*n*-Capryloyl chloride)

$CH_3.(CH_2)_6.C{=}O$ with Cl on the C $C_8H_{15}OCl$ Beil. II - 348, II_1—, II_2-(303)

B.P.			F.P.			
195.55°	at 760 mm.	(1)	−61.1°	(1) cf. (19)	D^2_4 = 0.94483	(1)
194–195°	at 756 mm.	(2)	−63° to −62.5° cor. (19)			
188–192°		(3)			D^{20}_4 = 0.94866	(1)
91°	at 22 mm.	(4)				
83°	at 16 mm.	(5) (19)			D^{15}_4 = 0.95349	(1)
74–77°	at 11 mm.	(6)				
[**104–105°**	at 9 mm.	(18)]			$n^{15}_{He\alpha}$ = 1.43408	(1)

Care must be taken not to confuse $\bar{C}$, the acid chloride of *n*-caprylic acid, with the corresponding relatives of *n*-caproic acid (C_6) and of *n*-capric acid (C_{10}); for this reason the name *n*-octanoyl chloride is preferred.

[For prepn. of $\bar{C}$ from *n*-octanoic acid (*n*-caprylic acid) (1:1145) with PCl_5 (yield: 82% (19), 64% (7), with PCl_3 (2) (8), with $PCl_3 + ZnCl_2$ (90% yield (7)), with $SOCl_2$ (3) (96% yield (6)), or with oxalyl (di)chloride (3:5060) (18) see indic. refs.]

[For use of $\bar{C}$ in prepn. of corresp. cellulose esters see (9) (10); for use in syntheses of glycerides see (11) (12); for use with $AlCl_3$ in Friedel-Crafts synthesis of various ketones see (13) (14) (19); for use in prepn. of derivatives of vanillylamine see (4) (16); for cat. hydrogenation to octanaldehyde (1:0192) see (15).]

[$\bar{C}$ with $AlCl_3$ + phenol yields (17) 45% *o*-(*n*-octanoyl)phenol, m.p. 22.3°, b.p. 169–170° at 11 mm., $D^{24}_4 = 0.9989$, $n^{25.5}_D = 1.5169$ (17) (semicarbazone, m.p. 157–158° (17)), and 38% *p*-(*n*-octanoyl)phenol, m.p. 62°, b.p. 224–225° at 10 mm. (17) (benzoate, m.p. 107–108° (17)).]

$\bar{C}$ on hydrolysis yields *n*-octanoic acid (*n*-caprylic acid) (1:1145) q.v. (for the amide, anilide, *p*-toluidide, and other derivs. corresponding to $\bar{C}$ see 1:1145).

3:8680 (1) Deffet, *Bull. soc. chim. Belg.* **40**, 389–394 (1931). (2) Henry, *Bull. acad. roy. Belg.* (3) 37, 63–70 (1899); *Cent.* **1899**, I 968; *Rec. trav. chim.* **18**, 252–253 (1899). (3) Bardan, *Bull.*
(5) Krafft,
89 (1939).
48 (1898).
929; *Cent.*
1929, II 2743.
(11) Heiduschka, Schuster, *J. prakt. Chem.* (2) **120**, 155–156 (1928). (12) Robinson, Roche, King, *J. Am. Chem. Soc.* **54**, 705–710 (1932). (13) Hartung, Munch, Deckert, Crossley, *J. Am. Chem. Soc.* **52**, 3320 (1930). (14) Ralston, Bauer, *J. Org. Chem.* **5**, 165–170 (1940). (15) Escourrou, *Bull. soc. chim* (5) **6**, 1181 (1939). (16) Nelson, *J. Am. Chem. Soc.* **41**, 2124 (1919). (17) Sandulesco, Girard, *Bull. soc. chim.* (4) **47**, 1309–1310 (1930). (18) Averill, Roche, King, *J. Am. Chem. Soc.* **51**, 868 (1929). (19) Paquette, Lingafelter, Tartar, *J. Am. Chem. Soc.* **65**, 686 (1943).

[illegible] (7) Kharasch, [illegible] *J. Org. Chem.* 3, 188-189 (1939). (8) Paal, Müller-
[illegible] hin, *Z. physik. Chem.* A-187, 181
[illegible]
[illegible] 9 (1929). (12) Radziszewski, *Ber.*
[illegible] (14) Evans, Mabbott, Turner, *J.
Chem. Soc.* 1927, 1159-1160, 1162-1163. (15) Darapsky, *J. prakt. Chem.* (2) 146, 257 (1936).
[illegible]

Ann. 430, 157 (1923).
(21) Smith (to Naugatuck Chem. Co.), U.S. 1,687,903, Oct. 16, 1928; Brit. 298,152, Oct. 4, 1927; *Cent.* 1929, I 2922; *C.A.* 23, 156 (1929). (22) Klages, Keil, *Ber.* 36, 1632 (1903). (23) I.G., French 729,730, July 30, 1932; *Cent.* 1932, II 3015. (24) Dorough (to du Pont Co.), U.S. 1,892,386, Dec. 27, 1932; *Cent.* 1933, I 2872; *C.A.* 27, 1897 (1933). (25) I.G., French 729,687, July 29, 1932; *Cent.* 1932, II 3015 (26) Naugatuck Chem Co., French 721,843, March 8, 1932; *Cent.* 1932, II 2109. (27) Zal'kind, Berkovich, Amusin, Russ. 34,547, Feb. 28, 1934; *Cent.* 1935, I 3347. (28) Fabr. de Laire, Ger. 268,786, Jan. 2, 1914, *Cent.* 1914, I 589. (29) Kharasch, Kleiman, *J. Am. Chem. Soc.* 65, 13-44 (1943).

3:8670 2,2-DICHLORO-OCTANE $C_8H_{16}Cl_2$ Beil. I - 160
I_1—
I_2—

$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2—\overset{Cl}{\underset{Cl}{C}}—CH_3$$

B.P. 190-200° (1)

[For prepn. of $\bar{C}$ from octanone-2 (*n*-hexyl methyl ketone) (1:5490) with PCl_5 see (1).]

3:8670 (1) Dachauer, *Ann.* 106, 271 (1858).

3:8675 4-CHLORO-1,2-DIMETHYLBENZENE C_8H_9Cl Beil. V - 363
(*unsym.*-Chloro-*o*-xylene)
V_1—
V_2—

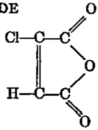
B.P. 195° u.c. (1) F.P. −6.25° (2) D_{15}^{15} = 1.0602 (4)
194° at 755 mm. (2)
192.2-194.0° (3)
191.5° cor. (4)
75.6-75.8° at 15 mm. (3)

[For prepn. of $\bar{C}$ from 4-amino-1,2-dimethylbenzene (*unsym.-o*-xylidine) [Beil. XII-1103, XII_1-(480)] via diazotization and use of Cu_2Cl_2 reaction see (2) (3); for prepn. of $\bar{C}$ from *o*-xylene (1:7430) with Cl_2 in pres. of I_2 (4) (1) or Fe (5) (1) (the isomeric 3-chloro-1,2-dimethylbenzene (3:8645) and other products are also formed) see indic. refs.]

$\bar{C}$ on oxidn. with hot dil. HNO_3 (D = 1.2) or by htg. with HNO_3 (D = 1.1) in a s.t. at 160° yields (4) (5) a mixt. of 5-chloro-2-methylbenzoic acid (3:4670), m.p. 130°, and 4-chloro-2-methylbenzoic acid (3:4700), eas. volatile with steam, ndls. from aq. or dil. AcOH (6), m.p. 170° (5) (6).

$\bar{C}$ added to 3-4 vols. HNO_3 (D = 1.5) in the cold, then htd. ½ hr. at 100°, then poured into aq. yields (2) 4-chloro-5-nitro-1,2-dimethylbenzene, m.p. 63° (2) (7). [Note (*a*) that small amt. of a dinitro cpd., m.p. 111° (2), is also formed; (*b*) that the prod. of m.p. 73° so obtd. by earlier work (1) was certainly impure; and (*c*) that the isomeric 3-nitro-4-chloro-1,2-dimethylbenzene has m.p. 75° (7).]

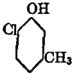
—— CHLOROMALEIC ANHYDRIDE C_4O_3Cl Beil. XVII-434
XVII$_1$—



B.P. 196° cor. M.P. 33–34° $D_4^{15} = 1.5427$

See 3:0280. *Division A: Solids.*

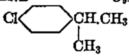
—— 6-CHLORO-3-METHYLPHENOL C_7H_7OCl Beil. VI —
VI$_1$-(187)
VI$_2$-(355)



B.P. 196° M.P. 46° $D_-^{15} = 1.215$

See 3:0700. *Division A: Solids.*

3:8705 4-CHLORO-ISOPROPYLBENZENE $C_9H_{11}Cl$ Beil. V - 395
(*p*-Chlorocumene) V$_1$—
V$_2$-(307)



B.P. 195–197° at 750 mm. (1)	D_{20}^{20} = 1.0257	(2)	n_D^{25} = 1.514	(1)
81° at 15 mm. (2)	1.0022	(1)		
66–72° at 11 mm. (7)	1.0190	(7)	n_D^{20} = 1.5120	(2)
			1.5109	(7)

The first reference given in Beil. V-395 *is erroneous.*

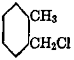
[For prepn. of $\bar{C}$ from β-(*p*-chlorophenyl)propene (2) by cat. hydrogenation see (2); from chlorobenzene (3:7903) with isopropyl alc. (1:6135) + H_2SO_4 (72% yield) see (3) or with isopropyl alc. (1:6135) + BF_3 + P_2O_5 (63% yield) see (7); for formn. of $\bar{C}$ from isopropylbenzene (cumene) (1:7440) with Cl_2 (together with other prods.) (4) (5) or with SO_2Cl_2 + $AlCl_3$ (6) see indic. refs.]

$\bar{C}$ on oxidn. with HNO_3 (D = 1.2) yields (3) (4) *p*-chlorobenzoic acid (3:4940).

$\bar{C}$ with chlorosulfonic acid yields a sulfonyl chloride which with NH_3 yields a sulfonamide, probably 2-chloro-5-isopropylbenzenesulfonamide, m.p. 91° (2).

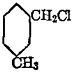
3:8705 (1) [illegible] 4929, *C.A.* **33**, 4587 (19[illegible] [illegible]eyer, Bernhauer, *Mon*[illegible] [illegible] 8, No. 4, 30 pp. (1934); *Cent.* **1934**, II 595; **1936**, I 540; *C.A.* **29**, 6885 (1935). (5) Varma, Srinivasan, *J. Indian Chem. Soc.* **13**, 191 (1936). (6) Töhl, Eberhard, *Ber.* **26**, 2944 (1893). (7) Hennion, Pieronek, *J. Am. Chem. Soc.* **64**, 2751–2752 (1942).

3:8710 *o*-XYLYL CHLORIDE C_8H_9Cl Beil. V - 364
(*o*-Methylbenzyl chloride, V$_1$-(180)
ω-chloro-*o*-xylene) V$_2$-(283)



B.P. 197–199° (1)
92–94° at 20 mm. (2)
76–80° at 14 mm. (3)

3:8700 **m-XYLYL CHLORIDE** (*m*-Methylbenzyl chloride, ω-chloro-*m*-xylene) C_8H_9Cl Beil. V - 373, V_1-(183), V_2-(291)



B.P. 195–196° u.c. (2) D_{20}^{20} = **1.064** (2) n_D^{25} = **1.5327** (1)
85–88° at 16 mm. (6)

[For special study of prepn. (76% yield) by chlorination of *m*-xylene (1:7420) in light see (1).]

C̄ stood with $N/10$ alc. NaOEt at 30° yields ethyl *m*-xylyl ether [Beil. VI-494], b.p. 202°, to extent of 10.9% in 6 hrs., 32.4% in 24 hrs. (3) cf. (4). [For data on rate of hydrolysis with acid or alkali in acetone soln. at 30° see (5).]

C̄ with Mg in ether yields R.MgCl; on carbonation at 0° (7) this yields *m*-$CH_3.C_6H_4.CH_2$.-COOMgCl; this upon acidification presumably (no record) would yield *m*-tolylacetic acid [Beil. IX-528], m.p. 61°; upon treatment (8) with C_2H_5MgBr, however, it gives a mixt. contg. 57.6% *m*-tolylmalonic acid, colorless pdr. from $CHCl_3$, m.p. 130–131° with loss of CO_2 (8). [Use of isopropyl MgCl in place of C_2H_5MgBr gave 88% of *m*-tolylmalonic ac. (8).]

C̄ on boiling with $Pb(NO_3)_2$ soln. (2), or $Cu(NO_3)_2$ soln. (30% yield (6)), or alk. Na_2CrO_4 (90% yield (6)) gives *m*-tolualdehyde (1:0208).

Ⓓ *N*-(*o*-Xylyl)phthalimide [Beil. XXI-467]: ndls. from alc., m.p. 117–118°. [Reported (9) from *m*-xylyl bromide and therefore presumably obtainable under appropriate conditions from C̄.]

3:8700 (1) King, Merriam, *Proc. Nova Scotian Inst. Sci.* **18**, 276–281 (1933/34); *C.A.* **29**, 6214 (1935); *Cent.* **1935**, II 2359. (2) Gundelach, *Bull. soc. chim.* (2) **26**, 43 (1876). (3) Franzen, *J. prakt. Chem.* (2) **97**, 83–84 (1918) (4) Olivier, *Rec. trav. chim.* **41**, 306–307 (1921). (5) Olivier, Weber, *Rec. trav. chim.* **53**, 885 (1934). (6) Posner, Schreiber, *Ber.* **57**, 1131, 1137 (1924). (7) Ivanoff, Spassoff, *Bull. soc. chim.* (4) **9**, 20 (1931). (8) Ivanoff, Pchenitchny, *Bull. soc. chim.* (5) **1**, 227 (1934). (9) Brömme, *Ber.* **21**, 2700 (1888).

3:8703 **ETHYL *d,l*-γ-CHLORO-*n*-VALERATE** $C_7H_{13}O_2Cl$ Beil. II - 302, II_1-(131), II_2—

$$CH_3.\underset{\displaystyle Cl}{\underset{|}{C}}H.CH_2.CH_2.COOC_2H_5$$

B.P. 196° (1) D_4^{20} = **1.0393** (1) n_D^{20} = **1.4310** (1)
70.5° at 9 mm. (2)

Oil with odor like amyl acetate.

[For prepn. of C̄ from γ-chloro-*n*-valeric acid (3:9270) + EtOH + H_2SO_4 see (1); from γ-*n*-valerolactone (1:5080) with HCl in EtOH see (3).] [For the opt. active isomers of C̄ see Beil. II_2-(268) and subsequent literature.]

3:8703 (1) Schjanberg, *Ber.* **70**, 2385–2391 (1937). (2) Wohlgemuth, *Compt. rend.* **158**, 1578 (1914); *Ann. chim.* (9) **2**, 300–301 (1914). (3) Noyes, Cox, *J. Am. Chem. Soc.* **25**, 1094 (1903).

87% (10) (11), 74% (6)) or warming in dimethylaniline (91% yield (1)) (17) (for intermediate formn. of β-phenylethyl chlorosulfite see (18)) see indic. refs.]

[For formn. of C̄ from β-chloroethyl p-toluenesulfonate with C_6H_5MgBr (36% yield (19)) (20) see indic. refs.; from di-(β-chloroethyl) sulfate with C_6H_5MgBr (25% yield) see (21); from C_6H_5HgCl with ICl in CCl_4 (35% yield) see (11); from methyl β-phenylethyl ether (22) or N-(β-phenylethyl)benzamide (7) (15) or N,N-*bis*-(β-phenylethyl)benzamide (60% yield (23)) with PCl_5 see indic. refs.; from β-phenylethylamine hydrochloride with HNO_2 see (24); from *bis*-(β-phenylethyl) ether with AcCl + $ZnCl_2$ see (9); from boilg. ethylbenzene (1:7410) with Cl_2 (as by-product of the α-isomer) see (25) (26) (27) (35).]

C̄ on oxidn. with CrO_3/H_2SO_4 is much more resistant than benzyl chloride (3:8535) (28) but ultimately yields benzoic acid (1:0715), m.p. 121°. — [C̄ passed with steam and air at 450° over pumice impregnated with V_2O_5 gives (29) benzoic acid (52%), benzaldehyde (35%), phenylacetaldehyde (6%), and styrene (3%).]

[C̄ on reduction with H_2 + $Pd/CaCO_3$ in pres. of MgO ultimately gives ethylbenzene (1:7410) but rate is very much slower than with α-chloroethylbenzene (3:8667) (12).]

[For study of rate of reactn. of C̄ with aq. alc. NaOH (much slower than with α-chloroethylbenzene (3:8667) see (10); for rate with NaOEt see (30); for rate with NaOPr see (47); C̄ with KOC_6H_5 in alc. gives (45–50% yield (31)) phenyl β-phenylethyl ether [Beil. VI-479], b.p. 180° at 23 mm., D_4^{20} = 1.0501 (31); C̄ with NaOAc + AcOH yields (32) mainly β-phenylethyl acetate (1:3922), but 15% of the isomeric *methyl-phenyl-carbinyl* acetate [Beil. VI-476, VI₁-(236)], b.p. 222° (32), is also formed.]

[C̄ with NaI in acetone boiled 4 hrs. gives (33) β-phenylethyl iodide, b.p. 125–128° at 18–20 mm. (33) (for rate of reactn. of C̄ with KI in acetone see (13) (34)): C̄ with alc. KCN yields (25) (26) (27) β-phenylethyl cyanide [Beil. IX-512, IX₁-(199)] which on hydrolysis gives hy[illegible] acid (1:0615), m.p. 48–49°; C̄ on boilg. for 20 hrs. with conc. aq. Na_2SO_3 gives [illegible] chloride, m.p. 34° [illegible] m.p. 77° (35)) ac[illegible] evolution of SO_2 (contrary to previous report (36)).]

C̄ with Mg in dry ether yields (2) (11) (19) (5) (37) (38) $C_6H_5.CH_2.CH_2.MgCl$: this RMgCl cpd. with dry CO_2 yields (19) hydrocinnamic acid (1:0615), m.p. 48–49°; with phenylisocyanate it yields (2) hydrocinnamanilide, m.p. 96°; with $HgCl_2$ it gives (85% yield (11)) β-phenylethyl HgCl, m.p. 163–166° (11). [For reactn. of this RMgCl cpd. with cyclopentanone (38), cyclohexanone (37), α-tetralone (37), and other ketones see indic. refs.]

[C̄ with $AlCl_3$ in CS_2 or lgr. gives (12) (1) a resin; *C̄ with $AlCl_3$ + C_6H_6 gives (85% yield* (39)) (40) dibenzyl (1:7149) together with other products (26) (27).] — [C̄ with Na in C_6H_6 or ether (41) gives ethylbenzene (1:7410) and 1,4-diphenylbutane [Beil. V-616, V₁-(290)], m.p. 52°.] [For behavior of C̄ with benzhydryl sodium (42), triphenylmethyl sodium, etc. (6), see indic. refs.]

[C̄ on mononitration, e g., with HNO_3 (D = 1.52) at −15° (3) (24) (4) (44) (45) or even at −70° (45) gives (70% yield (44)) β-(4-nitrophenyl)ethyl chloride, m.p. 49° (3) (44), 48–49° (4), 48° (45) (43), 46–47° (24), accompanied by (30% yield (44)) β-(2-nitrophenyl)-ethyl chloride, an oil, b.p. 156.5–158° at 15 mm., D_{-}^{20} = 1.5620, n_D^{20} = 1.562 (46); some β-(2,4-dinitrophenyl)ethyl chloride, m.p. 136° (4), is sometimes formed (4).]

3:8712 (1) Sisido, Kato, *J. Soc. Chem. Ind. Japan* **43**, Suppl. bind., 450–451 (1940); *C.A.* **35**,
3 [illegible] *J. Chem.*
[illegible]

Lachrymatory oil.

[For prepn. (88% yield) from *o*-tolylcarbinol (1:5922) by action of thionyl chloride and pyridine see (2), by action of H_2SO_4 + HCl (85–92% yield) see (3); the prepn. from *o*-xylene (1:7430) by action of trioxymethylene + HCl gives a mixture of C̄ and *p*-xylyl chloride (3:8660) (4) (5) (6).]

C̄ stood with $N/10$ alc. NaOEt at 30° yields ethyl *o*-xylyl ether [Beil. VI-484], oil, b.p. 208–210°, to extent of 21% in 6 hrs., 52% in 24 hrs. (7) cf. (8). [For data on rate of hydrolysis with acid or alkali in acetone soln. at 30° see (9).]

C̄ with Mg in ether yields R.MgCl; on carbonation at 0° (10) this yields *o*-$CH_3.C_6H_4.CH_2$.COOMgCl; this upon acidification presumably (no record) would yield *o*-tolylacetic acid [Beil. IX-527], m.p. 88–89°; upon treatment (11) with C_2H_5MgBr, however, it gives 83.3% yield of *o*-tolylmalonic ac., ndls. from aq., m.p. 139–140°, with loss of CO_2 (11), + 16% yield of *o*-tolylacetic ac.

C̄ refluxed 5 hrs. with dil. alc. KCN gives 74% yield (2) *o*-tolylacetonitrile [Beil. IX-527], b.p. 244°, which on boiling 1 hr. with dil. H_2SO_4 (2) gives 73% yield (2) of *o*-tolylacetic ac. [Beil. IX-527], ndls. from aq., m.p. 88–89°.

C̄ on warming at 100° with 1.3 moles pyridine gives ppt. of *o*-xylylpyridinium chloride, cryst. from CH_3OH + dry ether, m.p. 183° (12).

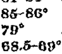
Ⓓ *N*-(*o*-Xylyl)phthalimide [Beil. XXI-467]: cryst. from alc., m.p. 148–149°. [Reported (13) from *o*-xylyl *bromide* and therefore presumably obtainable under appropriate conditions from C̄.]

3:8710 (1) Reyman, *Bull. soc. chim.* (2) **26**, 534 (1876). (2) Hill, Short, *J. Chem. Soc.* **1935**, 1125. (3) Reichstein, Cohen, Ruth, Meldahl, *Helv. Chim. Acta* **19**, 415 (1936). (4) Darzens, *Compt. rend* **208**, 818–820 (1939). (5) Shorygin, Skoblinskaya, *J. Gen. Chem.* (*U.S.S.R.*) **6**, [illegible] **31**, 2196 (1937) (6) Hoch, *Compt. rend* **192**, 1465 [illegible] **97**, 83 (1918). (8) Olivier, *Rec. trav chim.* **41**, 306 [illegible] *n.* **53**, 885 (1934). (10) Ivanoff, Spassoff, *Bull. soc. chim.* (4) **9**, 20 (1931).

(11) Ivanoff, Pchenitchny, *Bull. soc. chim.* (5) **1**, 226 (1934). (12) von Braun, Nelles, *Ber.* **70**, 1762 (1937). (13) Strassmann, *Ber.* **21**, 576 (1888).

3:8712 β-CHLOROETHYLBENZENE

(ω-Chloroethylbenzene, β-phenylethyl chloride, benzylcarbinyl chloride)

CH_2 CH_2Cl

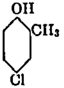
C_8H_9Cl Beil. V-(354) V_1-(177) V_2-(277)

B.P.			B.P. (*contd.*)			
197–198°		(1)	88°	at 16 mm.	(9)	D_4^{25} = 1.069 (14)
192–198° dec. at 760 mm.		(2)	82–84°	at 16 mm.	(2)	
190–200° sl. dec.		(3)	83–84°	at 14 mm.	(10)	n_D^{20} = 1.5294 (11)
96°	at 23 mm.	(4)	81–84°	at 14 mm.	(11)	
91–92°	at 20 mm.	(3) (5)	85–86°	at 12 mm.	(5)	
80°	at 20 mm.	(6)	79°	at 12 mm.	(12)	
94–96°	at 18 mm.	(7)	68.5–69°	at 4 mm.	(13)	
89–92°	at 16 mm.	(8)				

Colorless oily liquid.

[For prepn. of C̄ from β-phenylethyl alc. (1:6505) with fumg HCl in s.t. 4 hrs. at 140° (57% yield (13)) (15), with conc. HCl + $ZnCl_2$ (82% yield (8)), with 6 N HCl (small yield (16)), with PCl_5 in $CHCl_3$ (yield 70% (3)) (10) (12) (prod. conts P compounds (10) removed with $NaHCO_3$ (12)) or in CCl_4 (80% yield (5)), with $SOCl_2$ at room temp. (yields:

3:0780 4-CHLORO-2-METHYLPHENOL (4-Chloro-o-cresol)



C_7H_7OCl Beil. VI - 350 VI_1-(174) VI_2-(332)

M.P. 48–49° (1) (5) **B.P.** 220–225° (1) (2) (5)
45° (2)

Ndls. (from pet. eth.).

[For prepn. from o-cresol (1:1400) by chlorination with SO_2Cl_2 see (1) (5).]

$\bar{C}$ dislvd. in 5 pts. AcOH and treated with small excess of conc. HNO_3 (D = 1.42) yields (3) 6-nitro-4-chloro-2-methylphenol [Beil. VI_1-(178)], yel. ndls., m.p. 107° (3), eas. sol. alc., C_6H_6, less sol. AcOH, acetate, m.p. 88° (3).

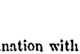
$\bar{C}$ htd. with phthalic anhydride (1:0725) + NaCl.$AlCl_3$ at 150–200° for 2 hrs. yields (4) after decompn. with HCl, and repeated recrystn. from C_6H_6, AcOH, xylene, 1-hydroxy-2-methyl-4-chloroanthraquinone, yel.-br. cryst., m.p. 177–179° (4).

$\bar{C}$ htd. with KOH + CH_3I yields (1) 4-chloro-2-methylanisole, volatile with steam, b.p. 212.6–214.6° cor. at 758 mm. (1).

Ⓓ **4-Chloro-2-methylphenyl benzoate**: from $\bar{C}$ + BzCl + aq. NaOH; lfts. from pet. eth., m.p. 71–72° (1).

3:0780 (1) Peratoner, Condorelli, *Gazz. chim. ital.* **28**, I 211 (1898). (2) Klarmann, Shternov Gates, *J. Am. Chem. Soc.* **55**, 2585 (1933). (3) Zincke, *Ann.* **417**, 222–223 (1918). (4) Waldmann, Sellner, *J. prakt. Chem.* **150**, 152 (1938). (5) Sah, Anderson, *J. Am. Chem. Soc.* **63**, 3165 (1941).

3:0810 1,6-DICHLORONAPHTHALENE (2,5-Dichloronaphthalene)



$C_{10}H_6Cl_2$ Beil. V - 543 V_1-(262) V_2-(446)

M.P. 49° (1) (2)
48.5–49° (3)
48° (4) (5) (9) (12) (13) (18) (19)
47–48° (11)

Ndls. from alc. — Volatile with steam. — Sublimes.

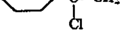
[For prepn. of $\bar{C}$ from naphthalenedisulfonic acid-1,6 [Beil. XI-213] (16), from K salt of 6-chloronaphthalenesulfonic acid-1 [Beil. XI-161] (4), from 6-chloronaphthalenesulfonyl chloride-1 [Beil. XI-161] (7), from 6-bromonaphthalenesulfonyl chloride-1 [Beil. XI-165] (8), from 5-chloronaphthalenesulfonyl chloride-2 [Beil. XI-180] (7), from 5-nitronaphthalenesulfonyl chloride-2 [Beil. XI-186] (9), from 6-chloronaphthol-1 (3:2615) (5), or from naphthalene-1,6-*bis*-(sulfonyl chloride) [Beil. XI-214] (10) (3) (6) by htg. with PCl_5 as directed see indic. refs.; for prepn. of $\bar{C}$ from 5-chloronaphthalenesulfonyl chloride-1 or 6-chloronaphthalenesulfonyl chloride-1 (both above) by htg. at 210–250° see (7); for prepn. of $\bar{C}$ from 6-chloronaphthylamine-2 via diazotization and use of Cu_2Cl_2 reactn. see (2); from 6-sulfonaphthylamine-1 [Beil. XIV-758, XIV_1-(735)] or from 5-sulfonaphthylamine-2 [Beil. XIV-748, XIV_1-(733)] via treatment of corresp. diazonium salt with PCl_5 in PCl_3 see (11); from 1,6-diaminonaphthalene [Beil. XIII-204] by tetrazotization in HCl and htg. with Cu pdr. (24% yield (3)) (12) (13) see indic. refs.; for prepn. of $\bar{C}$ from 1,6-dichloronaphthalenedisulfonic acid-4,8 [Beil. XI-213] or from 1,6-dichloronaphthalenedisulfonic acid-3,8 [Beil. XI-214] via hydrolysis of the $-SO_3H$ group by htg. with dil. H_2SO_4 in s.t.

(11) Whitmore, Thorpe, *J. Am. Chem. Soc.* **55**, 785 (1933). (12) Paal, Müller-Lobeck, *Ber.* **64**, 2148–2150 (1931). (13) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 241, 249 (1924). (14) Dunstan, Hilditch, Thole, *J. Chem. Soc.* **103**, 140 (1913). (15) von Braun, Deutsch, *Ber.* **45**, 1268–1269 (1912). (16) Norris, Watt, Thomas, *J. Am. Chem. Soc.* **38**, 1078 (1916). (17) Darzens, *Compt. rend.* **152**, 1316 (1911). (18) Carré, Libermann, *Compt. rend.* **198**, 274–276 (1934). (19) Gilman, Beaber, *J. Am. Chem. Soc.* **45**, 842 (1923). (20) Ashworth, Burkhardt, *J. Chem. Soc.* **1928**, 1798–1799.

(21) Suter, Evans, *J. Am. Chem. Soc.* **60**, 537 (1938). (22) Madinaveitia, *Bull. soc. chim.* (4) **25**, 604 [illegible] (1924). (24) Shoesmith, Connor, *J. Chem. Soc.* **1927** [illegible]–247 (1870). (26) Schramm, *Monatsh.* **8**, 104–105 [illegible]scher, Schmitz, *Ber.* **39**, 2209–2210 (1906). (28) Cou[illegible]). (29) Shoruigin, Losev, *J. Gen. Chem.* (*U.S.S.R.*) **3**, 821–824 (1933); *Cent.* **1934**, II 2206; *C.A.* **28**, 6103 (1934). (30) Kindler, *Ann.* **452**, 119–120 (1927).

[illegible]

Chem. **8**, 199–200 (1943).

3:8715 α-CHLOROVINYLBENZENE  C_8H_7Cl Beil. V - 476
(α-Chlorostyrene) V_1-(230) V_2-(367)

B.P.			F.P.
199°		(1)	−24° to −23° (5)
83.5–84°	at 23 mm.	(2)	
85.0–85.5°	at 22.5 mm.	(3)	
80–83°	at 21 mm.	(13)	
73°	at 16 mm.	(4)	
73–74°	at 15 mm.	(3)	
64°	at 9 mm.	(5)	

$D_4^{24.6} = 1.0983$ (2) $n_D^{24.6} = 1.55898$ (2)
$D_4^{20} = 1.101$ (2)
1.0975 (3)
1.0916 (3)
$n_D^{20.5} = 1.5584$ (5)
$D_4^{18} = 1.12$ (4)
$n_D^{20} = 1.5600$ (13)
$n_D^{18} = 1.5645$ (4)
$n_D^{17} = 1.56199$ (2)
$D_4^{17} = 1.1030$ (2)
$D_4^{15.6} = 1.1024$ (2)
$n_D^{15.5} = 1.56226$ (2)

Colorless liq. with arom. odor soon changing to that of formaldehyde and benzoyl chloride from air oxidation (5). — $\bar{C}$ could not be polymerized even in u.v. light, by peroxides or $SnCl_4$ (12).

[For prepn. of $\bar{C}$ from methyl phenyl ketone (acetophenone) (1:5515) with PCl_5 see (2) (1) (5) (6), from α,α-dichloroethylbenzene ("acetophenone dichloride") on htg. see (7); from β-bromo-α-chloroethylbenzene (styrene chloro-bromide) with alc. KOH in the cold (70% yield) see (4); from α,β-dichloroethyl benzene (styrene dichloride) (3:6685) with aq. alc. NaOH at 50–60° (89% yield) see (13).]

$\bar{C}$ on boilg. with conc. HCl (4) (1), or $\bar{C}$ with 80% H_2SO_4 at 60° for 4 hrs. (13) cf. (14), gives (81% yield (13)) cf. (14) acetophenone (1:5515).

$\bar{C}$ is resistant to actn. of alc. KOH (5); $\bar{C}$ on refluxing for 13 hrs. with very conc. alc. NaOEt gives (8) some phenylacetylene (1:7425) together with other prods. (8).

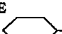
[$\bar{C}$ with NOCl yields (9) α,β,β-trichlorostyrene, b.p. 148–150° at 20 mm. (9); $\bar{C}$ htd. with alc. KCN in s.t. at 200–220° yields (10) phenylsuccinonitrile which on saponification gives phenylsuccinic acid (1:0790); $\bar{C}$ with Na in liq. NH_3 gives (15% yield (10)) ethylbenzene (1:7410); $\bar{C}$ with $NaNH_2$ in liq. NH_3 gives (57% yield (11)) phenylacetylene (1:7425); $\bar{C}$ in alc. contg. BF_3/EtOAc (12) or in pres. of HCl (1) condenses with itself by loss of 3 HCl yielding 1,3,5-triphenylbenzene (1:7270).]

$\bar{C}$ (10 g.) in C_6H_6 (10 ml.) stood 3 days with PCl_5 (30 g.) in C_6H_6 (50 ml.), then poured into aq. worked up as directed (13), yields 1-phenyl-1-chloroethylenephosphinic acid-2, $C_6H_5—C(Cl)=CH—P(=O)(OH)_2$, ndls. from dil. HCl, m.p. 162° (13) (together with a little benzoic acid (1:0715), m.p. 121°).

3:8715 (1) Béhal, *Bull. soc. chim.* (2) **50**, 632–638 (1888). (2) von Auwers, *Ber.* **45**, 2799–2801 (1912). (3) Ley, Rinke, *Ber.* **56**, 776 (1923). (4) Urion, Namias, *Bull. soc. chim.* (5) **3**, 2335–2336 (1936). (5) Dufraisse, Viel, *Bull. soc. chim.* (4) **37**, 878–879 (1925). (6) Taylor, *J. Chem Soc.* **1937**, 304–308. (7) Friedel, *Ann. chim.* (4) **16**, 360 (1869). (8) Nef, *Ann.* **308**, 269–270 (1898). (9) Perrot, *Compt. rend.* **202**, 495 (1936). (10) Vaughn, *J. Am. Chem. Soc.* **56**, 2064 (1934).
(11) Vaughn, Vogt, Nieuwland, *J. Am. Chem. Soc.* **56**, 2121 (1934). (12) Marvel, Moon, *J. Am. Chem. Soc.* **62**, 48 (1940). (13) Emerson, Agnew, *J. Am. Chem. Soc.* **67**, 518–520 (1945). (14) Emerson (to Monsanto Chem. Co.), U.S. 2,372,562, March 27, 1945; *C.A.* **39**, 3555 (1945).

3:8717 β-CHLOROVINYLBENZENE C_8H_7Cl Beil. V - 476

(β-Chlorostyrene, ω-chlorostyrene, styryl chloride)

—CH=CHCl

V₁-(230)
V₂-(367)

B.P.			B.P. (*contd.*)				
199–199.2°		(1)	**92–93°**	at 22 mm.	(5)	D_4^{25} = **1.1040**	(1)
199°	at 766 mm.	(2)	**88–100°**	at 18 mm.	(20)	n_D^{25} = **1.5736**	(1)
197–199°		(3)	**83°**	at 18 mm.	(6)	**1.5719**	(20)
195.5–196.5°	at 715 mm.	(4)	**89°**	at 17 mm.	(7) (1)	**1.5700**	(20)
113°	at 44 mm.	(1)	**82–87°**	at 16 mm.	(20)	D_4^{20} = **1.109**	(9)
112°	at 40 mm.	(2)	**83–84°**	at 11 mm.	(8)	**1.108**	(9)
			79.5°	at 11 mm.	(9)	D_4^{15} = **1.1122**	(1)
			78.5°	at 9 mm.	(9)	n_D^{15} = **1.5808**	(1)

Liquid with odor of hyacinth; used in perfume industry. Although $\bar{C}$ should exist in two geom. stereoisomeric forms only this one has as yet been recognized. — Volatile with steam.

[For prepn. of $\bar{C}$ from cinnamic acid (1:0735) with Cl_2/aq. or HOCl (1) (3) (10) (8) (12), with Cl_2 in EtOH (11), with NaOCl (13) (20), or $Ca(OCl)_2$ (14) see indic. refs.; from α,β-dichlorohydrocinnamic acid (cinnamic acid dichloride) [Beil. IX-514, IX₁-(200)] with Na_2CO_3 at 100° (yield: 97% (15) (1)) (9) (6) or with NaOAc (60% yield (5)) see indic. refs.; from α-chloro-β-hydroxyhydrocinnamic acid [Beil. X-250, X₁-(110)] by htg. with aq. in s.t. at 200–220° see (2) cf. (3): for formn. of $\bar{C}$ from ω,ω-dichloroethylbenzene [Beil. V-354] with alc. KOH in s.t. at 120° see (4); from phenyl-trichloromethyl-carbinol [Beil. VI-476, VI₁-(237)] with Zn dust in alc. see (16); from α,β-dichloroethylbenzene (styrene dichloride) (3:6685) by htg. with pyridine (17) or by passing over Al_2O_3 at 360–400° and 85–105 mm. (92% yield (20)) see indic. refs.; from C_6H_5MgBr with acetylene tetrachloride (3:5750) see (18): from styrene chlorohydrin (3:9570) by dehydration over HPO_3 on silica gel at 370–400° and 95–115 mm. (63% yield) see (20).]

[$\bar{C}$ with Cl_2 in $CHCl_3$ yields (1) α,β,β-trichloroethylbenzene [Beil. V-355], b.p. 254.5–255.5° sl. dec. at 770 mm., b.p. 137° at 21 mm., D_4^{15} = 1.3619, n_D^{15} = 1.5652 (1); $\bar{C}$ with

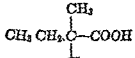
Br_2 in $CHCl_3$ yields (1) (13) (19) β-chloro-α,β-dibromoethylbenzene [Beil. V-356], ndls. from alc., m.p. 32° (1) (13), b.p. 165° sl. dec. at 26 mm. (1).

C̄ with alc. KOH in s.t. at 200–250° is partly resinified (2); C̄ with very conc. alc. KOH gives on very strong htg. a chlorine-free oil which on distn. with aq. gives phenylacetaldehyde (1:0200) (4). [For rate of loss of halogen with alc. KOH see (5).] — C̄ with EtOH/NaOEt in s.t. at 175–182° for 5½ hrs. gives (66% yield (20)) β-ethoxystyrene [Beil. VI-564, VI_1-(279)] for conversion of which to phenylacetaldehyde see (20).]

C̄ on oxidn. with $K_2Cr_2O_7$ + H_2SO_4 or with HNO_3 (D = 1.2) gives (2) benzoic acid (1:0715).

3:8717 (1) Biltz, *Ann.* **296**, 266–268, 272–273 (1897). (2) Glaser, *Ann* **154**, 164–167 (1870). (3) Forster, Saville, *J. Chem. Soc.* **121**, 2595–2600 (1922). (4) Forster, *Ber.* **17**, 982–983 (1884). (5) Dann, Howard, Davies, *J Chem. Soc.* **1928**, 609–610. (6) Durrans, *J. Chem. Soc.* **123**, 1427 (1923). (7) Bergmann, *J. Chem. Soc* **1936**, 404. (8) Farmer, Hose, *J. Chem. Soc.* **1933**, 964. (9) von Auwers, *Ber.* **45**, 2796–2797 (1912). (10) Erlenmeyer, Lipp, *Ann.* **219**, 185–186 (1883).
(11) Jackson, Pasiut, *J. Am. Chem Soc.* **49**, 2074 (1927). (12) Böeseken, *Rec. trav. chim.* **41**, 204 (1921). (13) Ssuknewitsch, Tschilingarjan, *Ber.* **68**, 1214 (1935). (14) Stenhouse, *Ann.* **55**, 3–4 (1845). (15) Erlenmeyer, *Ber.* **14**, 1868 (1881). (16) Jozitsch, Favorski, *J. Russ. Phys.-Chem. Soc.* **30**, 920–924 (1898), *Cent.* **1899**, I 607. (17) I.G., French 729,730, July 30, 1932; *Cent.* **1932**, II 3015. (18) Swarts, *Bull. soc. chim.* (4) **25**, 168–169 (1919). (19) Reich, van Wijck, Waelle, *Helv. Chim Acta* **4**, 248 (1921) (20) Emerson, Agnew, *J. Am. Chem. Soc.* **67**, 518–520 (1945)

3:8718 d,l-α-CHLORO-α-METHYL-n-BUTYRIC ACID $C_5H_9O_2Cl$ Beil. II-306 II_1— II_2—



B.P. 200–205° at 754 mm., sl. dec. (1) **$D_{?}^{10}$ = 1.101 (1) $n_{?}^{11}$ = 1.45077 (1)**
123–124° at 36 mm. (1)

Oily liq.; insol. aq.; sol. alc, ether.

[For prepn of C̄ from α-chloro-α-methyl-n-butyronitrile by hydrolysis with conc. HCl see (1).]

—— Methyl α-chloro-α-methyl-n-butyrate: unreported.
—— Ethyl α-chloro-α-methyl-n-butyrate (see 3:8518).
—— α-Chloro-α-methyl-n-butyramide: unreported.
—— α-Chloro-α-methyl-n-butyranilide: unreported.
—— α-Chloro-α-methyl-n-butyro-p-toluidide: unreported.

3:8718 (1) Servais, *Rec trav. chim.* **20**, 58–59 (1901).

3:8719 1-CHLORONONANE $CH_3.(CH_2)_7.CH_2Cl$ $C_9H_{19}Cl$ Beil. I— (n-Nonyl chloride) I_1— I_2-(128)

B.P.			
202° at 760 mm. (4)	D_{25}^{25} = 0.8931 (3)	n_D^{25} = 1.4400 (3)
98–100° at 22 mm. (1)	D_{20}^{20} = 0.8679 (1)	n_D^{20} = 1.43692 (1)
92.6–93.0° at 16 mm. (2)	D_4^{20} = 0.8704 (4)	1.43400 (4)
76–79° at 4 mm. (3)		

[For prepn. of C̄ from nonanol-1 (1:6265) + PCl_3 + $ZnCl_2$ (53% yield) or PCl_5 + $ZnCl_2$ in C_6H_6 (58% yield) or excess $SOCl_2$ (76% yield (4)) in C_6H_6 (62% yield) see (1);

for prepn. of C̄ (52% yield (3)) from *n*-hexyl MgBr + γ-chloro-*n*-propyl *p*-toluenesulfonate see (3).]

3:8719 (1) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (2) Kohlrausch, Koppl, *Monatsh.* **63**, 269 (1933). (3) Rossander, Marvel, *J. Am. Chem. Soc.* **50**, 1495 (1928). (4) Vogel, *J. Chem. Soc.* **1943**, 638, 640.

3:8720 1,6-DICHLOROHEXANE $C_6H_{12}Cl_2$ **Beil. I - 144**
(Hexamethylene dichloride) I_1—
I_2-(109)

Cl Cl
| |
$CH_2.CH_2.CH_2.CH_2.CH_2.CH_2$

B.P. 203–205° (1)
94° at 22 mm. (2)

[For prepn. of C̄ from *N,N'-bis*-benzoylhexamethylenediamine [Beil. IX-263] via reactn. with PCl_5 and distn. of the resultant *bis*-(imide chloride) (64% yield (2)), or similarly from *N*-(benzoyl)hexamethyleneimine [Beil. XX_1-(27)] (3), see (2) (3); for formn. from hexamethylenediamine [Beil. IV-269] with NOCl (1) or from hexanediol-1,6 diphenyl ether [Beil. VI-148] by htg. with HCl in s.t. at 165–175° see (1).]

Ⓓ Hexanediol-1,6 diphenyl ether (1,6-diphenoxyhexane) [Beil. VI-148]: cryst. from alc., m.p. 83° (2), 83.0–83.5° cor. (3). [From C̄ on refluxing 12½ hrs. with large excess sodium phenolate in alc. (2) (41% yield (3))]. [The half reactn. prod., ω-chloro-*n*-hexyl phenyl ether [Beil. VI-144], is an oil, b.p. 164–165° at 11 mm. (4).]

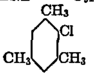
3:8720 (1) Solonina, *J. Russ. Phys.-Chem. Soc.* **30**, 606–632 (1898); *Cent.* **1899**, I 25. (2) von Braun, *Ber.* **38**, 2344–2345 (1905). (3) Müller, Sauerwald, *Monatsh.* **48**, 732 (1927). (4) von Braun, Müller, *Ber.* **39**, 4112–4113 (1906).

—— **β-CHLOROPROPIONIC ACID** $Cl.CH_2.CH_2.COOH$ $C_3H_5O_2Cl$ **Beil. II - 249**
II_1-(111)
II_2-(226)

B.P. 204° **M.P. 42°**

See 3:0460. *Division A: Solids.*

3:8725 2-CHLORO-1,3,5-TRIMETHYLBENZENE $C_9H_{11}Cl$ **Beil. V - 408**
(*eso*-Chloromesitylene) V_1—
V_2-(315)



B.P. 204–206° (1) $D^{30}_{-} = 1.0337$ (2) $n^{30}_D = 1.52119$ (2)
103.6–103.7° at 25 mm. (2)
90–91° at 20 mm. (3)

C̄ remains liquid down to −20°. C̄ is insol. aq., eas. sol. alc. or ether; volatile with steam but less so than dichloromesitylene.

[For prepn. of C̄ from 1,3,5-trimethylbenzene (mesitylene) (1:7455) with Cl_2 either directly (1) or in $CHCl_3$ at 0° (75% yield (3)) accompanied by 2,4-dichloro-1,3,5-trimethylbenzene (1) and/or 2,4,6-trichloro-1,3,5-trimethylbenzene, m.p. 209° (3), 204–205° (1)), or from 2,4,6-trimethylphenol (mesitol) (1:1467) with PCl_5 in C_6H_6 (2) see indic. refs.]

C̄ with fumg. H_2SO_4 (20% SO_3) shaken for 15 min. gives 2-chloromesitylenesulfonic acid

(corresp. sulfonyl chloride, oil (3), sulfonamide, m.p. 165.5–166° (3)) but gives no evidence of any Jacobsen rearrangement (3).

C̄ with fumg. HNO_3 yields (1) (4) mainly 4,6-dinitro-2-chloromesitylene, colorless ndls. from alc., m.p. 178–179° (1), 176.5° (4) [the mononitration prod., 4-nitro-2-chloromesitylene, has m.p. 56–57° (1)].

C̄ on oxidn. with boilg. dil. HNO_3 (1 conc. HNO_3: 2 aq.) for 30 hrs. yields (1) 4-chloro-3,5-dimethylbenzoic acid ("chloromesitylenic acid") [Beil. IX-536], browns at 220° but does not melt (unsuitable as derivative). [Note that a little 4-nitro-2-chloromesitylene m.p. 56–57° (1), may be formed in this process; furthermore that attempts to oxidize C̄ with $K_2Cr_2O_7$ + dil. H_2SO_4 yield only acetic acid (1).]

C̄ on oxidn. with aq. $KMnO_4$ gives (63.5% yield (5)) 2-chlorobenzenetricarboxylic acid-1,3,5 (chlorotrimesic acid) (3:4975), readily sol. cold aq., excessively sol. hot aq., m.p. anhydrous acid 285° (5), monohydrate 278° (6).

3:8725 (1) Fittig, Hoogewerff, *Ann.* **150**, 323–329 (1869). (2) Brown, de Bruyne, Gross, *J. Am. Chem. Soc.* **56**, 1291 (1934). (3) Smith, Moyle, *J. Am. Chem. Soc.* **58**, 1, 4, 7 (1936). (4) Anschutz, Boedeker, *Ann.* **454**, 108 (1927). (5) Davies, Wood, *J. Chem. Soc.* **1928**, 1126–1127. (6) Ost, *J. prakt. Chem.* (2) **15**, 310 (1877).

3:8727 ETHYL δ-CHLORO-*n*-VALERATE $C_7H_{13}O_2Cl$ Beil. II - 302

$CH_2.CH_2\,CH_2\,CH_2\,COOC_2H_5$ (with Cl on the first CH_2) II₁— II₂-(268)

B.P. 205–206°	(1)	
120–125° at 40 mm.	(2)	n_D^{20} = 1.4355 (4)
93° at 16 mm.	(5)	
83.5–85° at 8 mm.	(4)	
83° at 8 mm.	(3)	

[For prepn. of C̄ from δ-chloro-*n*-valeric acid (3:0075) with EtOH + dry HCl see (1) (2) (3) (4); from δ-ethoxy-*n*-valeryl chloride (5) on htg. with 0.7% conc. H_2SO_4 at 100° for 5 hrs see (5).]

[For reactn. of C̄ with diethyl sodio-ethylmalonate see (2); for rate of reactn. of C̄ with KI in acetone at 50° see (3).]

Neither C̄ nor its halogen is rapidly hydrolyzed by cold aq. 10% NaOH (3) (use in sepn. of C̄ from phenol (3)).

3:8727 (1) Funk, *Ber.* **26**, 2574–2575 (1893). (2) Mellor, *J. Chem. Soc.* **79**, 132 (1901). (3) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 244–245, 249 (1924). (4) Cheney, Piening, *J. Am. Chem. Soc.* **67**, 733 (1945). (5) Prelog, Heimbach-Juhasz, *Ber.* **74**, 1704 (1941).

3:8730 ISOAMYL β-CHLOROPROPIONATE $C_8H_{15}O_2Cl$ Beil. II —

iso-$C_5H_{11}O.CO.CH_2.CH_2Cl$ II₁-(111) II₂-(227)

B.P. 207–208° at 740 mm. (1)	D_4^{20} = 1.0171 (3)	n_D^{20} = 1.4343 (3)
121° at 30 mm. (4)		
87° at 12 mm. (2)	D_4^{15} = 1.0419 (4)	n_D^{11} = 1.4380 (4)

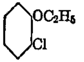
[For prepn. (97% yield (2), 90% yield (1)) from isoamyl alc. (1:6200) + β-chloropropionic ac. (3:0460) see (1) (2).]

C̄ on htg. at 220° with diethylaniline gives (poor yield (4)) isoamyl acrylate, b.p. 157–159° at 756 mm., n_D^{12} = 1.4287 (4).

Ⓓ **Isoamyl β-(phthalimido)propionate:** from C̄ in 70% yield on htg. with potassium phthalimide in s.t. at 130° for 1 hr.; prod. repeatedly extracted with dry ether and solvent evapd.; cryst. from alc., m.p. 61° (1). [This product on shaking with 12 pts. HBr (48%) at 40° yields β-phthalimidopropionic acid (40% yield), cryst. from aq., m.p. 150–151° (4).]

3:8730 (1) Hale, Britton, *J. Am. Chem. Soc.* **41**, 844–845 (1919). (2) Fichter, Schnider, *Helv. Chim. Acta* **14**, 857 (1931). (3) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935). (4) Moureu, Murat, Tampier, *Ann. chim.* (9) **15**, 247, 251 (1921).

3:8735 *o*-CHLOROPHENETOLE (*o*-Chlorophenyl ethyl ether)



C_8H_9OCl Beil. VI - 184 VI—

B.P. 210.3°	(1)	D_4^{25} = **1.1288**	(5)	n_D^{25} = **1.5284**	(5)
208°	(2)	$D_{24.2}^{24.2}$ = **1.12993**	(1)	$n_{H\alpha}^{24.2}$ = **1.52333**	(1)
97–98° at 15 mm.	(5)			$n_{H\beta}^{24.2}$ = **1.54014**	(1)

Colorless oil, volatile with steam.

[For prepn. from 3-chloro-4-ethoxyaniline [Beil. XIII-511, $XIII_1$-(181)] by replacement of $-NH_2$ group with H via diazo reaction see (3).]

C̄ added dropwise to 2 pts. HNO_3 (D = 1.38) with cooling, then poured into aq., yields (3) 2-chloro-4-nitrophenetole [Beil. VI-240], yel. ndls. from alc. + lgr., m.p. 82° (3).

Ⓓ **3-Chloro-4-ethoxybenzenesulfonamide:** cryst. from dil. alc., m.p. 132–133° u.c. (4). [From C̄ by treatment with chlorosulfonic ac. followed by conversion of the intermediate sulfonyl chloride to the sulfonamide by treatment with $(NH_4)_2CO_3$ (73% yield (4)).] [Note that this prod. depresses the m.p. of the corresponding deriv. (m.p. 134–134.5°) from *p*-chlorophenetole (3:0090) (4).]

3:8735 (1) Swarts, *J. chim. phys.* **20**, 75–76 (1923). (2) Beilstein, Kurbatow, *Ann.* **176**, 39 (1875). (3) Reverdin, Düring, *Ber.* **32**, 155–156 (1899). (4) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603–604 (1940). (5) Anzilotti, Curran, *J. Am. Chem. Soc.* **65**, 609 (1943).

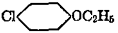
—— ***d,l*-α-CHLORO-ISOVALERIC ACID** $C_5H_9O_2Cl$ Beil. II - 316 II_1— II_2—

$CH_3.CH.CH.COOH$ (with CH_3 on the CH and Cl on the CH.COOH)

B.P. 210–212° at 756 mm. **M.P. 16°** $D_{-}^{13.2}$ = **1.135** n_{-}^{11} = **1.44496**

See 3:0050. *Division A: Solids.*

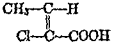
—— ***p*-CHLOROPHENETOLE**



C_8H_9OCl Beil. VI - 187 VI_1-(101) VI_2-(176)

B.P. 211.6° cor. **M.P. 20–21°** $D_{20.2}^{20.2}$ = **1.12310** n_D^{19} = **1.5227**

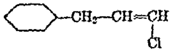
See 3:0090. *Division A: Solids.*

—— α-CHLOROCROTONIC ACID  $C_4H_5O_2Cl$ Beil. II - 414
II_1-(189)
II_2-(395)

B.P. 212° M.P. 99–100°

See 3:2760. *Division A: Solids.*

3:8737 1-CHLORO-3-PHENYLPROPENE-1 C_9H_9Cl Beil. V —
(ω-Chloroallylbenzene; V_1—
γ-chloroallylbenzene) V_2-(373)



B.P. 212–214° cor. (1) $D_4^{14} = 1.073$ (1) $n_D^{14} = 1.545$ (1)
97° at 18 mm. (1)
76° at 13 mm. (2)

Liquid with penetrating odor suggesting benzene.

[For prepn. of C̄ from 1,3-dichloropropene-1 (3:5280) with $C_6H_6 + AlCl_3$ (3), or with C_6H_5MgBr in toluene (1) (4) or ether (2) (alm. quant. yield (1)), see indic. refs.]

C̄ with PCl_5 gives on warming (by addition to C̄ of 2 atoms chlorine) alm. quant. yield (5) of 3-phenyl-1,1,2-trichloropropane, b.p. 135–136° at 13 mm., $D_4^{23} = 1.293$, $n_D^{23} = 1.553$ (5).

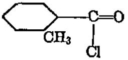
C̄ with Br_2 adds similarly giving (1) (4) 1-chloro-1,2-dibromo-3-phenylpropane, b.p. 160° at 12 mm., $D_4^{10} = 1.727$, $n_D^{10} = 1.611$ (4) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (6)).

[C̄ resists hydrolysis and is unchanged even after several hours with aq. + PbO in s.t. at 200° (1) (4); however, C̄ with KOH (3 moles) in abs. alc. on refluxing at 130–135° is readily converted (by reactn. of the ω-chlorine atom and rearr. or vice versa) into cinnamyl ethyl ether (γ-ethoxyallylbenzene) [Beil. VI-571, VI_1-(281)], b.p. 127–128° at 22 mm., $D_4^{15} = 0.970$, $n_D^{15} = 1.547$ (1) (4), which by cleavage with HCl under press. gives (7) cinnamyl chloride (3:0010) q v.]

[C̄ with Na (4 moles) in boilg. toluene gives (8) propenylbenzene (β-methylstyrene) [Beil. V-481, V_1-(371)], b.p. 176°, neither methyl phenylacetylene nor benzylacetylene being formed.]

[C̄ with $NaNH_2$ in high-boilg. pet. at 105–110° gives (75% yield (9)) (10) (11) benzylacetylene [Beil. V_2-(408)], b.p. abt. 166° at 760 mm. (with resinification).]

3:8737 (1) Bert, *Bull. soc. chim.* (4) **37**, 879–881 (1925). (2) von Braun, Kühn, *Ber.* **58**, 2171 (1925). (3) Bert, *Compt rend* **213**, 619–620 (1941); *Cent* **1942**, II 30–31; *C.A.* **37**, 4373 (1943). (4) Bert, *Compt. rend.* **180**, 1504–1506 (1925). (5) Bert, Annequin, *Compt. rend.* **192**, 1107–1108 (1931). (6) Bert, *Compt. rend.* **215**, 356–357 (1942); *C A.* **38**, 3633 (1944). (7) Bert, Dorier, [illegible] t, Raynaud, [illegible] Bert, Dorier, [illegible] –193 (1927).

3:8740 o-TOLUYL CHLORIDE (o-Methylbenzoyl chloride)  C_8H_7OCl Beil. IX - 464 IX_1-(187)

B.P.			B.P. (contd.)		
213.0–213.6°	at 760 mm.	(1)	110–111°	at 29 mm.	(7)
213°	at 760 mm.	(2)	109–123°	at 28 mm.	(8)
212°	at 762 mm.	(3)	99–100°	at 12 mm.	(9)
212° cor.		(4)	99–103°	at 11 mm.	(10)
211°	at 733 mm.	(5)	83°	at 8 mm.	(26)
206–208°		(6)	75.6°	at 5.5 mm.	(11)
			75.0–75.5°	at 2 mm.	(12)

[For prepn. of C̄ from o-toluic acid (1:0690) with PCl_5 (10) (yield: 100% (3), 75% (13)), with PCl_5 in $CHCl_3$ (7), with PCl_3 at 110° (14), with $POCl_3$ (6) or $POCl_3$+ alk. chloride (15), with $SOCl_2$ (11) (yield: 100% (9), 95% (2), 92% (26), 89% (4)) see indic. refs.; for prepn. of C̄ from o-toluic anhydride (see below) with PCl_5 in $POCl_3$ see (7).]

C̄ with pyridine + excess $K_2S_2O_5$ yields (16) o-toluic anhydride, m.p. 39° (16) (7), 36–37° (17).

[For Friedel-Crafts reactn. of C̄ + $AlCl_3$ + various hydrocarbons to yield corresp. ketones, e.g., with C_6H_6 (5) (6) (18), with toluene (19), with naphthalene (9), with phenanthrene (20), with acenaphthene (4), etc., see indic. refs.; C̄ with MeZnI gives (75% yield (21)) methyl o-tolyl ketone.]

[For studies of rate of reactn. of C̄ with MeOH (22) (23), with EtOH (12) see indic. refs.]

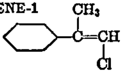
[For actn. of Br_2 on C̄ see (2); for reactn. of C̄ with diethyl sodiomalonate see (24); for sulfonation of C̄ see (25); for behavior of C̄ with C_6H_5MgBr in ether + $CoBr_2$ see (26).]

C̄ on hydrolysis yields o-toluic acid (1:0690), m.p. 104° (for the amide, anilide, p-toluidide, and other derivatives corresp. to C̄ see 1:0690).

3:8740 (1) Kohlrausch, Pongratz, Stockmair, *Monatsh.* **67**, 107 (1936). (2) Davies, Perkin, *J. Chem. Soc.* **121**, 2207 (1922). (3) van Scherpenzeel, *Rec. trav. chim.* **20**, 169 (1901). (4) Guyer, Zuffanti, *J. Am. Chem. Soc.* **57**, 1787–1788 (1935). (5) Ador, Filliet, *Ber.* **12**, 2301 (1879). (6) Reddelien, *Ber.* **48**, 1468 (1915). (7) Klages, Lickroth, *Ber.* **32**, 1561 (1889). (8) Hayashi, *J. prakt. Chem.* (2) **123**, 300 (1929). (9) Mayer, Fleckenstein, Gunther, *Ber.* **63**, 1470 (1930). (10) Cohen, Dudley, *J. Chem. Soc.* **97**, 1749 (1910).

(11) Thompson, Norris, *J. Am. Chem. Soc.* **58**, 1955 (1936). (12) Norris, Young, *J. Am. Chem. Soc.* **57**, 1420–1424 (1935). (13) Tanner, Lasselle, *J. Am. Chem. Soc.* **48**, 2164 (1926). (14) Frankland, Wharton, *J. Chem. Soc.* **69**, 1311 (1896). (15) Kissling (to I.G.), Ger. 642,519, March 10, 1937; *Cent.* **1937**, I 3874; *C.A.* **31**, 5816 (1937). (16) Gasopoulos, *Praktika Acad. Athenon* **6**, 347–353 (1931). (17) Adams, Wirth, French, *J. Am. Chem. Soc.* **40**, 426 (1918). (18) Diesbach, Strebel, *Helv. Chim Acta* **8**, 561 (1925). (19) Mauthner, *J. prakt. Chem.* (2) **103**, 393 (1921). (20) Clar, *Ber.* **62**, 358 (1929).

(21) Ruzicka, Ehmann, *Helv. Chim. Acta* **15**, 150 (1932). (22) Norris, Fasce, Staud, *J. Am. Chem. Soc.* **57**, 1415–1420 (1935). (23) Ott, *Ber.* **55**, 2123 (1922). (24) Mercer, Robertson, *J. Chem. Soc.* **1936**, 292. (25) Meiser (to General Aniline and Film Corp.), U.S. 2,273,974, Feb. 24, 1942; *C.A.* **36**, 3809 (1942). (26) Kharasch, Nudenberg, Archer, *J. Am. Chem. Soc.* **65**, 497 (1943).

3:8742 1-CHLORO-2-PHENYLPROPENE-1 (β-Chloro-α-methylstyrene)  C_9H_9Cl Beil. V - 485 V_1— V_2—

B.P. 213–215° (1)
210–215° (2)
102–106° at 14 mm. (2)

[For prepn. of C̄ from α,β-dichloroisopropylbenzene (α-methylstyrene dichloride) [Beil. V-395] with alc. KOH see (2); from β-chloro-α-hydroxyisopropylbenzene [Beil. VI-507] on distn. at ord. press. (3) or by htg with oxalic acid (2) see indic. refs.; from the lower-melting stereoisomer of β-methylcinnamic acid [Beil. IX-614, IX_1-(254)] with HOCl see (2).]

3:8742 (1) Tiffeneau, *Compt. rend.* **138**, 986 (1904). (2) Tiffeneau, *Ann. chim.* (8) **10**, 166, 173, 180 (1907). (3) Tiffeneau, *Compt. rend.* **134**, 775 (1902).

3:8745 γ,γ'-DICHLORO-DI-*n*-PROPYL ETHER $C_6H_{12}OCl_2$ **Beil. S.N. 24**
(*bis*-(γ-Chloro-*n*-propyl)ether)

$ClCH_2.CH_2.CH_2$
$\quad O$
$ClCH_2.CH_2.CH_2$

B.P. 215° at 745 mm. (1) D_{20}^{20} = **1.140** (1)
93–95° at 18 mm. (2)

[For prepn. (10–15% yield (1)) from trimethylene chlorohydrin (3:8285) by refluxing with dil. H_2SO_4 see (1).]

3:8745 (1) Kamm, Newcomb, *J. Am. Chem. Soc.* **43**, 2228–2229 (1921). (2) Eastman Org. Chem. List No. 33 (1942).

3:8765 PELARGONYL CHLORIDE $CH_3.(CH_2)_7.C{=}O$ (with Cl on C) $C_9H_{17}OCl$ **Beil. II - 353**
(*n*-Nonanoyl chloride) II_1—
II_2-(308)

B.P.	F.P.	
215.35° at 760 mm. (1)	**−60.5°** (1)	D_4^{25} = **0.93780** (1)
220° at 749 mm. (2)		D_4^{20} = **0.94206** (1)
98° at 15 mm. (3)		D_4^{15} = **0.94633** (1) n_{He}^{15} = **1.43802** (1)
93–96° at 11 mm. (4)		
89° at 6 mm. (5)		

[For prepn. of C̄ from pelargonic acid (*n*-nonanoic acid) (1:0560) with PCl_5 (3) (65% yield (6)), with PCl_3 (2) (72% yield (1)), with PCl_3 + $ZnCl_2$ (93% yield (6)), or with $SOCl_2$ (yield 93.5% (4), 85% (6)) see indic. refs.]

[For reactn. of C̄ with toluene + $AlCl_3$ to give corresp. ketone see (7), with $AlCl_3$ + anisole to give corresp. ketone see (8), with ethyl sodio-acetoacetate and hydrolysis to methyl *n*-octyl ketone (decanone-2) see (9), with K carbazole to yield *N*-(*n*-nonyl)carbazole, m.p. 72–73°, see (10), with vanillylamine see (5).]

[C̄ with $AlCl_3$ + phenol yields (11) 55% *o*-(*n*-nonanoyl)phenol, b.p. 180° at 10 mm., m.p. 18.4°, D_4^{24} = 0.9887, $n_D^{25.5}$ = 1.5130 (11) (semicarbazone, m.p. 164° (11), and 35% *p*-(*n*-nonanoyl)phenol, m.p. 54.5°, b.p. 232° at 10 mm. (benzoate, m.p. 99.8° (11)).]

C̄ on hydrolysis yields pelargonic acid (1:0560) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see 1:0560).

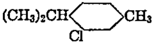
3:8765 (1) Deffet, *Bull. soc. chim. Belg.* **40**, 389–396 (1931). (2) Henry, *Bull acad roy. Belg.* (3) **37**, 63–72 (1899); *Cent* **1899**, I 968; *Rec. trav. chim.* **18**, 253–254 (1899). (3) Krafft, Koenig, *Ber.* **23**, 2384 (1890). (4) Fierz-David, Kuster, *Helv Chim. Acta* **22**, 86–89 (1939). (5) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 855 (1934). (6) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (7) Hasan, Stedman, *J. Chem. Soc.* **1931**, 2117. (8) Skraup, Nieten, *Ber.* **57**, 1302–1303 (1924). (9) Asahina, Nakayama, *J. Pharm. Soc. Japan* **1925**, No. 526, 3–5; *Cent.* **1926**, I 2670. (10) Copisarow, *J. Chem. Soc.* **113**, 818 (1918).
(11) Sandulesco, Girard, *Bull. soc. chim.* (4) **47**, 1310 (1930).

—— *p*-CHLOROBENZALDEHYDE  C_7H_5OCl Beil. VII - 235 VII_1-(133)

B.P. 214.5°–216.5° at 760 mm. M.P. 48–49°

See 3:0765. *Division A: Solids.*

3:8770 3-CHLORO-4-ISOPROPYL-1-METHYLBENZENE $C_{10}H_{13}Cl$ Beil. V - 423 V_1— V_2-(326)
(3-Chloro-*p*-cymene)



B.P. 217.1° at 760 mm. (1) D_4^{18} = 1.01799 (5)
213–214° cor. at 735.6 mm. (2) n_D^{18} = 1.51796 (5)
214° at 760 mm. (3)
120–122° at 20 mm. (4) (5)

[For prepn. of $\bar{C}$ from thymol (3-hydroxy-*p*-cymene) (1:1430) with PCl_5 see (1) (4) (5) (6); for prepn. of $\bar{C}$ from 2-bromo-*p*-cymene [Beil. V-423, V_1-(205)] by chlorination to 5-chloro-2-bromo-*p*-cymene [Beil. V-424] followed by replacement of Br by H with Zn/Cu at 200° (7) or in alc. alk. (8) see (7) (8); for prepn. of $\bar{C}$ from 3-chloromenthadiene dibromide by elimination of 2 HBr with quinoline see (3).]

[$\bar{C}$ on oxidn. with 15 pts boilg. dil. HNO_3 (D = 1.24) gives (2) a mixt. of 3-chloro-4-isopropylbenzoic acid (3-chlorocuminic acid) [Beil. IX-549], m.p. 122–123°, 2-chloro-4-methylbenzoic acid (2-chloro-*p*-toluic acid) (3:4355), m.p. 155°, and 2-chloroterephthalic acid (3:4995), m.p. about 320°.]

[$\bar{C}$ on mononitration with 6 pts. conc. HNO_3 (D = 1.48) below 15° for 3–4 hrs. as directed (4) yields 6-nitro-3-chloro-*p*-cymene = 2-nitro-5-chloro-*p*-cymene [Beil. V-424], oil, b p. 142–150° at 13 mm. (4) (which with piperidine for 30 min. at 100° yields (4) 2-nitro-5-piperdino-*p*-cymene, oil, b p 146–148° at 32 mm. (4)).]

$\bar{C}$ *on dinitration by adding to 10 pts. conc.* HNO_3 (D = 1.5) *below* −5° *during* 15 min, then poured onto ice, yields (4) (9) a mixt. from which can be isolated 2,6-dinitro-3-chloro-*p*-cymene, m.p. 105–106° (9), 102.5–103 5° (4) (which with piperidine (5 pts.) at 100° for 1½ hrs. yields 2,6-dinitro-3-piperidino-*p*-cymene, pale yel. ndls. from alc., m.p. 126–127° (9), 123–124° (4)).

[During this dinitration of $\bar{C}$ there is also formed a by-prod. formerly (4) supposed to be 2-chloro-3,5-dinitro-4-methylacetophenone but more recently (10) shown to be 3-chloro-4,6-dinitrotoluene, m.p. 90.0–90.5° (10); this prod. with piperidine gives (10) 3-piperidino-4,6-dinitrotoluene, m.p. 116–116.5° (10).]

3:8770 (1) Kobe, Okabe, Ramstad, Huemmer, *J. Am. Chem. Soc.* **63**, 3251–3252 (1941). (2) Fileti, Crosa, *Gazz. chim. ital.* **16**, 288 (1886). (3) Junger, Klages, *Ber.* **29**, 316 (1896). (4) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* **1934**, 848–852. (5) C. G. LeFevre, R. J. W. LeFevre, K. W. Robertson, *J. Chem. Soc.* **1935**, 483. (6) Vongerichten, *Ber.* **11**, 364–369 (1878). (7) [illegible] (8) Livak, Carlson [illegible] (9) Qvist, Moilanen, [illegible], II 1337–1338; *C.A.* [illegible] *hys.* **14**, *No.* 3, 9 pp.

at 180–200° see (1); *from 1,6-dichloronaphthalenesulfonyl chloride-3* [Beil. XI-182] (14) or from 1,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (18) by htg. with conc. HCl in s.t. at 290° see indic. refs., *from sodium α-naphthalenesulfonate* [Beil. XI-155, XI_1-(37)] with boilg. dil. HCl + $KClO_3$ (other products are also formed) see (15).]

[C̄ *on mononitration* in AcOH with fumg. HNO_3 yields (19) (20) 1,6-dichloro-4-nitronaphthalene [Beil. V-556], m.p. 119° (19).]

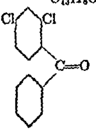
[C̄ on monosulfonation with mixt. of equal vols. conc. + fumg. H_2SO_4 (17) or with $ClSO_3H$ in CS_2 (18) gives 1,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-163] (corresp. sulfonyl chloride, m p. 151° (17) (18), corresp. sulfonamide, m.p. 216° (18)).]

[C̄ on oxidn. with dil. HNO_3 in s t at 150° yields (19) a mixt. of 3-chlorophthalic acid (3:4820) and 4-chlorophthalic acid (3:4390) together with their nitro derivs.]

3:0810 (1) Friedländer, Kielbasinski, *Ber.* **29**, 1980–1982 (1896). (2) Schroeter, *Ber.* **63**, 1318 (1930). (3) Hampson, Weissberger, *J Chem. Soc.* **1936**, 394. (4) Forsling, *Ber.* **20**, 2105 (1887). (5) Erdmann, Kirchhoff, *Ann* **247**, 379 (1888). (6) Ferrero, Bolliger, *Helv. Chim. Acta* **11**, 1146–1150 (1928). (7) Armstrong, Wynne, *Chem. News* **71**, 255 (1895). (8) Sindall, *Chem. News* **60**, 58 (1889). (9) Cleve, *Bull soc chim.* (2) **26**, 448 (1876). (10) Armstrong, Wynne, *Chem. News* **62**, 164 (1890).

(11) Erdmann, *Ann.* **275**, 214–215, 256, 279 (1893). (12) Friedlander, Szymanski, *Ber.* **25**, 2081 (1892) (13) Kehrmann, Matis, *Ber.* **31**, 2419 (1898). (14) Armstrong, Wynne, *Chem. News* **76**, 69 (1897) (15) Kozlov, Talybov, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1827–1833 (1939); *C.A.* **34**, 4067 (1940). (16) Zil'berman, Rashevaskaya, Martyntseva, *J Applied Chem.* (*U.S.S.R.*) **9**, 1832–1840 (1936), *Cent.* **1937**, I 4787, *C A.* **31**, 2597 (1937). (17) Cleve, *Ber.* **24**, 3177–3478 (1891). (18) Armstrong, Wynne, *Chem. News* **61**, 274–275 (1890). (19) Cleve, *Bull. soc. chim.* (2) **29**, 499 (1878). (20) Armstrong, Wynne, *Chem. News* **61**, 94 (1890).

3:0825 2,4-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. VII - 420
(2,4-Dichlorophenyl phenyl ketone) VII_1—



M.P. 48–49° (1) (2)
52° (3)

Cryst. (from alc. (1)).

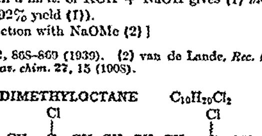
[For prepn. from *m*-dichlorobenzene (3:5960) + BzCl (3:6240) + $AlCl_3$ at 110–140° see (3) (2); for prepn. (67% yield (1)) from 2,4-dichlorobenzohydrol by oxidn. with CrO_3 in AcOH see (1)]

C̄ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) *m*-dichlorobenzene (3:5960) and BzOH (1:0715) (92% yield (1)).

[C̄ does not give a smooth reaction with NaOMe (2)]

3:0825 (1) Lock, Rödiger, *Ber.* **72**, 868–869 (1939). (2) van de Lande, *Rec. trav. chim.* **51**, 99, 105 (1932). (3) Böeseken, *Rec. trav. chim.* **27**, 15 (1908).

3:0840 2,7-DICHLORO-2,7-DIMETHYLOCTANE $C_{10}H_{20}Cl_2$ Beil. I —
I_1-(66)
I_2—



M.P. 40° (1)

3:8777 γ-PHENYL-*n*-PROPYL CHLORIDE $C_9H_{11}Cl$ Beil. V - 391

(γ-Chloro-*n*-propylbenzene, hydrocinnamyl chloride)  $CH_2.CH_2.CH_2.Cl$ V_1-(190) V_2-(305)

B.P. 219–220° cor. (1) (3) (13)		$D_4^{25} = 1.056$ (7)	$n_D^{25} = 1.52030$ (2)
106–106.5°	at 22 mm. (2)		1.5160 (6)
110°	at 21 mm. (3) (13)	$D_{-}^{25} = 1.04259$ (2)	
95–97°	at 12 mm. (10)		
93.5–95°	at 11 mm. (4)	$D_{25}^{25} = 1.0801$ (6)	
85–87°	at 9 mm. (5)		
89–93°	at 6 mm. (6)		

[For prepn. of C̄ from γ-phenyl-*n*-propyl alc. (hydrocinnamyl alc.) (1:6520) with fumg. HCl in s.t. at 130° (1) (15) or 140–150° (3), or in s.t. at 100° for 8 hrs. (77% yield (5)), or with $ZnCl_2$ + conc. HCl (40% yield (8)) (2) see indic. refs.; with $SOCl_2$ in ether (82% yield (9)) or pyridine (48.5% yield (10)) or dimethylaniline (70.5% yield (10)) see indic. refs. (for intermediate formn. of γ-phenyl-*n*-propyl chlorosulfite and *bis*-(γ-phenyl-*n*-propyl) sulfite in this reactn. see (11)); from γ-chloro-*n*-propyl *p*-toluenesulfonate (2 moles) with C_6H_5MgBr in ether (yield: 62% (6), 31% (12)) see indic. refs.; from $C_6H_5CH_2MgCl$ with di-(β-chloroethyl) sulfate in ether (66% yield) see (4); from *o*-(γ-chloro-*n*-propyl)-aniline via diazotization and treatment with alk. + $SnCl_2$ (75% yield (3)) (13) see indic. refs.; from *N*-methyl-*n*-(γ-phenyl-*n*-propyl)benzamide with PCl_5 see (14).]

C̄ is not decomposed on boilg. with $ZnCl_2$ and does not react at 100° with AgOAc (1).

[C̄ boiled for 8 hrs. with excess 5% NaOMe in MeOH gives (86% yield (15)) γ-phenyl-*n*-propyl methyl ether [Beil. VI_1-(252)], b.p. 206.5° at 758.5 mm. u.c., b.p. 100–102° at 20 mm. (15); C̄ with KOH in EtOH refluxed 2 hrs. gives (1) γ-phenyl-*n*-propyl ethyl ether [Beil. VI-503], b.p. 224° cor.; C̄ boiled several hours with excess conc. alc. $NaOC_6H_5$ gives (100% yield (3)) γ-phenyl-*n*-propyl phenyl ether [Beil. VI-504, VI_1-252], b.p. 182–183° at 17 mm. (3).]

[C̄ on boilg. several hours with alc. NaI yields (3) γ-phenyl-*n*-propyl iodide, b.p. 137–140° at 20 mm. (3) (for rate of reactn. of C̄ with KI in acetone at 50° see (5)).]

[C̄ with activated Mg in dry ether gives (98% yield (9)) $C_6H_5.CH_2\ CH_2.CH_2.MgCl$; for reactn. of this RMgCl cpd. with various carbonyl cpds., e.g., acrolein (10), ethyl phenyl ketone (9), or cyclopentanone (16), see indic. refs.]

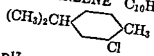
[C̄ with $AlCl_3$ in CS_2 or lgr. gives (17) about 10% hydrindene (1:7511), b.p. 177°, together with other products.]

[C̄ on mononitration with 4 vols. HNO_3 ($D = 1.5$) below −10° gives over 90% yield (18) of γ-(*p*-nitrophenyl)-*n*-propyl chloride [Beil. V_1-191], b.p. 176–180° at 15 mm. with sl. dec. (18).]

3:8777 (1) Errera, *Gazz. chim. ital.* **16**, 313–314 (1886). (2) Goebel, Wenzke, *J. Am. Chem. Soc.* **60**, 698 (1938). (3) von Braun, *Ber.* **43**, 2841–2842 (1910). (4) Suter, Evans, *J. Am. Chem. Soc.* **60**, 536–537 (1938). (5) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 242, 249 (1924). (6) Rossander, Marvel, *J. Am. Chem. Soc.* **50**, 1495 (1928). (7) Dunstan, Hilditch, Thole, *J. Chem. Soc.* **103**, 140 (1913). (8) Norris, Taylor, *J. Am. Chem. Soc.* **46**, 756 (1924). (9) Gilman, Harris, *J. Am. Chem. Soc.* **54**, 2075 (1932). (10) Cohen, *J. Chem. Soc.* **1935**, 433.

(11) Carré, Libermann, *Compt. rend.* **198**, 274–276 (1934). (12) Gilman, Beaber, *J. Am. Chem. Soc.* **45**, 842 (1923). (13) Merck, Ger. 239,076, Oct. 9, 1911; *Cent.* **1911**, II 1393. (14) von Braun, Aust, *Ber.* **49**, 507 (1916). (15) Straus, Berkow, *Ann.* **401**, 151 (1913). (16) Denissenko, *Ber.* **69**, 2186 (1936). (17) von Braun, Deutsch, *Ber.* **45**, 1269 (1912).

3:8775 **2-CHLORO-4-ISOPROPYL-1-METHYLBENZENE** $C_{10}H_{13}Cl$ Beil. V - 423 **3:8775**
(2-Chloro-*p*-cymene)



V₁—
V₂-(325)

B.P. **217.6°**
216–218° at 760 mm. (1)
216–218° cor. at 762 mm. (2) (3)
216–217° at 746 mm. (4)
215–218° at 761 mm. (5)
214–216° (6)
213–216° (7)
213–214° (8)
117° at 764 mm. (9)
103–105° at 35 mm. (4)
85–90° at 19 mm. (10)
at 5 mm. (6)

D_4^{17} = **1.0208** (5)
1.0152 (?) (2)

n_D^{17} = **1.51776** (5) (2)

[For prepn. of C̄ from carvacrol (2-hydroxy-*p*-cymene) (1:1760) with PCl_5 see (1) (11); from *p*-cymene (1:7505) with Cl_2 in pres. of I_2 (9) (3) (12) (8) (17) or Fe (6) (17) see indic. refs.; from 2-amino-*p*-cymene (cymidine) (carvacrylamine) [Beil. XII-1171, XII₁-(506)] via diazotization and use of Cu_2Cl_2 reactn see (2) (9); from carvone (1:5540) (13) or eucarvone [Beil. VII-151, VII₁-(99)] (13) or carvenone [Beil. VII-78, VII₁-(66)] (10) with PCl_5 (cf. (14) (15)) see indic. refs.]

C̄ on oxidn. with boilg. dil. HNO_3 yields (12) (8) (11) (10) 3-chloro-4-methylbenzoic acid (3-chloro-*p*-toluic acid) (3:4900), m.p. 199° (10), 196° (8), 194–195° (12).

C̄ on dinitration with 10–12 pts HNO_3 (D = 1.5) below 0° (2) (16) (18) or with a mixt. of conc. or fumg. HNO_3 + fumg. H_2SO_4 as directed (2) (8) (6) yields 5,6-dinitro-2-chloro-*p*-cymene, cryst. from AcOH (2), dil. AcOH (2), EtOH (6), or dil. MeOH (16), m.p. 111.0–111.5° cor (18), 109.5–110.5° (2), 109.5° (8), 108–109° (6) [This prod. refluxed with 5–10 pts. piperidine for 20–60 min at 100° gives 3,5-dinitro-2-piperidino-*p*-cymene, yel. ndls. from AcOH (2) or from dil. alc. (18) (16), m.p. 123–124° (16), 122.5–123.5° (18), 122–123° (2).] [Note that the original structure assigned by (6) to dinitro-C̄ has been confirmed by (18) despite intermediate contrary views (2) (16).]

[C̄ with Br_2 + Fe at ord. temp. yields (17) 5-bromo-2-chloro-*p*-cymene, b.p. 247° (17).]

3:8775 (1) Kobe, Okabe, Ramstad, Huemmer, *J. Am. Chem. Soc.* **63**, 3251–3252 (1941). (2) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* **1934**, 852–854. (3) Ganguly, R. J. W. LeFevre, *J. Chem. Soc.* **1934**, 1699. (4) Fileti, Crosa, *Gazz. chim. ital.* **18**, 299 (1888). (5) C. G. LeFevre, R. J. W. LeFevre, K. W. Robertson, *J. Chem. Soc.* **1935**, 480–488. (6) Lubs, Young, *J. Ind. Eng. Chem.* **11**, 1130–1133 (1919). (7) Junger, Klages, *Ber.* **29**, 315 (1896). (8) Hintikka, *Ann. Acad. Sci. Fennicae* **19-A**, No. 10, 6 pp. (1923), *C.A.* **19**, 42 (1925). (9) R. J. W. LeFevre, *J. Chem. Soc.* **1933**, 980–984. (10) Marsh, Hartridge, *J. Chem. Soc.* **73**, 854–855 (1898). (11) Fleischer, Kekulé, *Ber.* **6**, 1090 (1873). (12) Vongerichten, *Ber.* **10**, 1249–1252 (1877). (13) Klages, Kraith, *Ber.* **32**, 2554, 2558, 2560 (1899). (14) Semmler, *Ber.* **41**, 4478 (1908). (15) Wallach, *Ann.* **368**, 15 (1909). (16) R. J. W. LeFevre, *J. Chem. Soc.* **1933**, 980. (17) Varma, Srinivasan, *J. Indian Chem. Soc.* **13**, 190–191 (1936). (18) Qvist, Kajander, *Acta Acad. Aboensis, Math. et Phys.* **13**, No. 10, 16 pp. (1942); *Cent.* **1942**, II 26–28; *C.A.* **37**, 4370–4372 (1943).

— ***p*-CHLOROPHENOL**

C_6H_5OCl Beil. VI - 186
VI₁-(100)
VI₂-(174)

B.P. **218–219°** M.P. **42–43°**

See 3:0175 *Division A: Solids.*

3:8783 ***d,l-α*-CHLORO-*n*-VALERIC ACID** $C_5H_9O_2Cl$ Beil. II-302, II₁—, II₂—.

$CH_3.CH_2.CH_2.\underset{\displaystyle Cl}{CH}.COOH$

B.P.		F.P.		
222°	at 763 mm. (1)	−15° (1)	$D^{13.2}_{-}$ = **1.141** (1)	n^{11}_{-} = **1.44807** (1)
132–135° at	32 mm. (1)			

Oil; insol. aq., sol. in alc., ether.

[For prepn. of C̄ from *α*-chloro-*n*-valeronitrile by hydrolysis with conc. HCl see (1) (2).]

[The *levo*rotatory isomer of C̄, b.p. 80–84° at 1 mm., has been obtd. (3) from dextrorotatory 3-chlorohexene-1 by ozonolysis in $CHCl_3$, decompn. with aq., and Br_2/aq. oxidn. of the resultant aldehyde.]

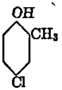
—— *α*-Chloro-*n*-valeramide: cryst. from alc. + aq. (3:1), m.p. 70–70.2° (4). [Prepd. indirectly from *α*-chloro-*n*-valeronitrile with conc. HCl (4).]

—— *α*-Chloro-*n*-valer-anilide: unreported.

—— *α*-Chloro-*n*-valero-*p*-toluidide: unreported.

3:8783 (1) Servais, *Rec. trav. chim.* **20**, 45–46 (1901). (2) Henry, *Bull. acad. roy. Belg.* (3) **36**, 241–262 (1898); *Cent.* **1898**, I 194. (3) Levene, Haller, *J. Biol Chem.* **83**, 596 (1929). (4) Vandewijer, *Bull. soc. chim. Belg.* **45**, 255 (1936).

—— **4-CHLORO-2-METHYLPHENOL** C_7H_7OCl *Beil. VI-(359)*, VI₁-(174), VI₂-(332)

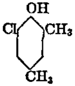


B.P. 220–225° **M.P. 48–49°**

See 3:0780. *Division A: Solids.*

3:8784 **6-CHLORO-2,4-DIMETHYLPHENOL** C_8H_9OCl Beil. VI-489, VI₁-(241), VI₂—

(5-Chloro-*m*-4-xylenol)

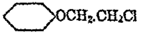


B.P. **221–223°** at 760 mm. (1)
100–101° at 17 mm. (2)
100–101° at 16 mm. (3)
86.5–87° at 9 mm. (2)

Oil with phenolic odor. — Sol. aq., eas. sol. org. solvents. — Volatile with steam.

[For prepn. of C̄ from 2,4-dimethylphenol (*unsym.-m*-xylenol) (1:1740) by chlorination with acet-*N*-chloro-2,4-dichloroanilide in AcOH contg. HCl at 15° as directed (1), or with SO_2Cl_2 in AcOH (3), see indic. refs.; from 6-amino-2,4-dimethylphenol hydrochloride [Beil. XIII-630, XIII₁-(245)] via diazotization and use of Cu_2Cl_2 reaction (77% yield) see (2); for formn. of C̄ from 2,4-dimethylquinol (*m*-xyloquinol) [Beil. VIII-22, VIII₁-(514)] by action of HCl (some of the isomeric 5-chloro-2,4-dimethylphenol (3:2460) also being formed) see (2) (4).]

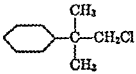
—— β-PHENOXYETHYL CHLORIDE C_8H_9OCl Beil. VI - 142
VI₁—
VI₂-(144)



B.P. 220° M.P. 28°

See 3:0165. *Division A: Solids.*

3:8780 NEOPHYL CHLORIDE (1) $C_{10}H_{13}Cl$ Beil. V —
(β-Chloro-*ter*-butyl)benzene; V_1—
(β-chloro-α,α-dimethyl)ethylbenzene V_2-(320)



B.P. 221° dec.	at 741 mm. (1)	n_D^{20} = 1.5250 (1)
111°	at 90 mm. (2)	1.5253 (3)
119–120°	at 30 mm. (3)	1.5248 (8)
104–105°	at 20 mm. (5)	
104–105°	at 18 mm. (4)	
97°	at 13 mm. (1)	
95°	at 10 mm. (1)	
53°	at 1 mm. (8)	

[For prepn. of C̄ from benzene (1:7400) + methallyl chloride (3-chloro-2-methylpropene-1) (3:7145) by condensation in presence of conc. H_2SO_4 (68% yield (1)) or HF (66% yield (2)) see (1) (2); for formn. from *ter*-butylbenzene (1:7460) by treatment with SO_2Cl_2 see (3); for formn. from corresp. alc. (2-methyl-2-phenylpropanol-1) with $SOCl_2$ see (5) (4).]

C̄ htd. with 13% alc. KOH at 86° for 24 hrs. is unchanged (2); C̄ refluxed 11½ hrs. with NaOEt in abs. alc. (1) or refluxed 9½ hrs. with pyridine (1) is recoverable to extent of 87–88% (1).

[For study of behavior of C̄ with Na, Na in liq. NH_3, NaEt, $NaNH_2$, etc., or on pyrolysis see (1).]

C̄ with sublimed Mg (not comml. Mg even after activation) + a trace of I_2 yields (3) neophyl MgCl; this RMgCl on oxidation with O_2 gives (71.6% yield (1)) the corresp alc., 2-methyl-2-phenylpropanol-1, b.p. 131° at 30 mm. (1), 122–123° at 20 mm. (5), n_D^{20} = 1.5261 (*N*-phenylcarbamate, m.p. 59–60° (5), 59.5–60.5° (1); *N*-(α-naphthyl)carbamate, m.p. 91.5–92.5° (1)). [For behavior of C̄ with C_6H_5MgBr in pres. of $CoBr_2$ see (8).]

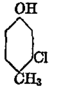
Ⓓ β-Phenylisovaleric acid: cryst. from pet. eth., m.p. 57.5–58.5° (6), 58–59.5° (1). [From RMgCl on carbonation and subsequent hydrolysis, yield 81.6% (1).]

Ⓓ β-Phenylisovaleranilide: m.p. 122–123° (3), 121–123° (6) [from RMgCl by reactn. with phenyl isocyanate (3)].

Ⓓ *p*-Acetamino-(β-chloro-*ter*-butyl)benzene: m.p. 155–156° (7). [From C̄ by nitration, reduction, and acetylation (7).]

3:8780 (1) Whitmore, Weisgerber, Shabica, *J. Am. Chem. Soc.* 65, 1469–1471 (1943). (2) Calcott, Tinker, Weinmayr, *J. Am. Chem. Soc.* 61, 1012 (1939) [illegible]
61, 2147–2148 (1939). (4) Haller, Ramart, C[illegible]
Haller, Bauer, *Ann. chim.* (9) 9, 10–14 (1918).
(7) Ipatieff, Schmerling, *J. Am. Chem. Soc.* 67, [illegible]
Soc. 66, 1438–1440 (1944).

—— 3-CHLORO-4-METHYLPHENOL



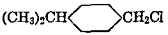
C_7H_7OCl

Beil. VI-402
VI_1—
VI_2—

B.P. 228° at 760 mm. M.P. 55°

See 3:1025. *Division A: Solids.*

3:8795 4-ISOPROPYLBENZYL CHLORIDE $C_{10}H_{13}Cl$ Beil. V - 423
(Cuminyl chloride; 1-chloromethyl-4-isopropylbenzene)



V_1—
V_2-(326)

B.P.		F.P.		
228° with part. dec.	(1)	−29° (8)	$D_4^{21.5}$ = 1.020 (1)	$n_D^{21.5}$ = 1.523 (1)
227–228°	(2)			
226–229°	(3)			
225–229°	(4)			
116–118° at 22 mm.	(5)			
110° cor. at 15 mm.	(1)			
108–109° at 14 mm.	(6)			
100° at 14 mm.	(7)			

Liq. with odor and lachrymatory effect less than that of benzyl chloride (3:8535) but with irritating effect on skin (1). — $\bar{C}$ on boilg. (4) (espec. in presence of $ZnCl_2$) partially dec. with formn. of a hydrocarbon $C_{20}H_{24}$ (probably 2,6-di-isopropyl-9,10-dihydroanthracene [Beil. V-654]), yel. pdr., m.p. 90° (4).

[For prepn. of $\bar{C}$ from *p*-isopropylbenzene (cumene) (1:7440) with trioxymethylene (75% yield (1)) or formalin (75% yield (7)) + HCl + $ZnCl_2$ see (1) (7); with chloromethyl methyl ether (3:7085) + $SnCl_4$ see (8); from *p*-cymeme (1:7505) by direct chlorination see (4) (3) (9); from cuminyl alc. [Beil. VI-543] with dry HCl (10) or const.-boilg. HCl (100% yield (2)) see (10) (2) (9).]

$\bar{C}$ with Zn + HCl reduces (10) to *p*-cymene (1:7507). — $\bar{C}$ on boilg. with aq. $Pb(NO_3)_2$ soln. (7) or alk. $Na_2Cr_2O_7$ (12) yields *p*-isopropylbenzaldehyde (cuminaldehyde) (1:0234). — $\bar{C}$ with aq. alk. presumably (no record) yields cuminyl alcohol [Beil. VI-543] but with alc. KOH gives (4) ethyl cuminyl ether [Beil. VI-544], b.p. 227° (4).

$\bar{C}$ with Mg in dry ether yields (9) cuminyl MgCl accompanied by some bicumyl (4,4'-diisopropyldibenzyl) [Beil. V-623], m.p. 58° (9); the R.MgCl with aq. gives (74% yield (1)) *p*-cymene (1:7505); the R.Mg.Cl upon treatment with O_2 gas gives (71–80% yield (9)) cuminyl alcohol [Beil. VI-543], b.p. 246° cor. (9), 140° at 20 mm. (9); the R.Mg.Cl with CO_2 gives (73% yield (9)) after acidification *p*-isopropylphenylacetic acid (homocuminic ac.) [Beil. IX-561], m p. 52°, b.p. 195° at 30 mm., 190° at 25 mm., D_4^{15} = 1.039, n_D^{15} = 1.522 (9). [The R.COOMgCl cpd. if treated with isopropyl MgCl gives mainly (11) *p*-isopropylmalonic ac., m.p. 143.5° dec. (1).]

3:8795 (1) Bert, *Bull. soc. chim.* (4) **37**, 1266–1268 (1925). (2) Norris, Mulliken, *J. Am. Chem. Soc.* **42**, 2098 (1920). (3) Varma, Srinivasan, *J. Indian Chem. Soc.* **13**, 191 (1936). (4) Errera, *Gazz. chim. ital.* **14**, 277–283 (1884). (5) Jones, *J. Chem. Soc.* **1938**, 1416. (6) Baker, Nathan, *J. Chem. Soc.* **1935**, 1844. (7) Blanc, *Bull. soc. chim.* (4) **33**, 317 (1923). (8) Darzens, Levy, *Compt. rend.* **194**, 2057 (1932). (9) Bert, *Bull. soc. chim.* (4) **37**, 1577–1583 (1925). (10) Paterno, Spica, *Gazz. chim. ital.* **9**, 397–398 (1879).

(11) Ivanoff, Pchénitchny, *Bull. soc. chim.* (5) **1**, 229 (1934). (12) Blanc, Ger. 347,583, Jan. 23, 1922; *Cent.* **1922**, II 1138.

[For studies of bactericidal action of C̄ see (3) (5).]

The nitration of C̄ has not been reported, and none of its mononitro- or dinitro-derivs. are known; for patent on sulfonation of C̄ see (6).

C̄ in alc. soln. with $FeCl_3$ gives olive-green color turning brown on htg.

—— 6-Chloro-2,4-dimethylphenyl acetate: unreported.

—— 6-Chloro-2,4-dimethylphenyl benzoate: oil (2).

Ⓓ 6-Chloro-2,4-dimethylphenyl *p*-nitrobenzoate: m.p. 94–94.5° (2). [From C̄ + *p*-nitrobenzoyl chloride in pyridine (2).]

Ⓓ 6-Chloro-2,4-dimethylphenyl *N*-phenylcarbamate: m.p. 129–130° (2). [From C̄ + phenyl isocyanate at 150–200° (2).]

3:8784 (1) Orton, King, *J. Chem. Soc.* **99**, 1191 (1911). (2) Bamberger, Reber, *Ber.* **46**, 793–795, 798–799 (1913). (3) Heicken, *Angew. Chem.* **52**, 263–265 (1939). (4) Bamberger, Reber, *Ber.* **40**, 2268 (1907). (5) Lockemann, Kunzmann, *Angew. Chem.* **46**, 296–301 (1933). (6) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; *Cent.* **1932**, II 2370–2371; [*C.A.* **27**, 735 (1933)].

3:8785 1-CHLORODECANE $CH_3.(CH_2)_8.CH_2Cl$ $C_{10}H_{21}Cl$ Beil. I - 169
(*n*-Decyl chloride) I_1—
I_2-(129)

B.P. 223.0–223.5°	at 760 mm. (1)	D_{25}^{25} = 0.8850 (4)	n_D^{25} = 1.4400 (4)
222–223°	at 760 mm. (7)	D_4^{20} = 0.8696 (1)	n_D^{20} = 1.43799 (1)
180–190°	at 720 mm. (2)	0.8683 (7)	1.43731 (7)
130–140°	at 80 mm. (3)	$D_4^{20.5}$ = 0.8621 (6)	$n_D^{20.5}$ = 1.4368 (6)
122°	at 50 mm. (2)		
137–142°	at 24 mm. (4)		
100.8–101.0°	at 12 mm. (5)		
106°	at 16 mm. (6)		

Colorless oil with characteristic odor (1).

[For prepn. of C̄ from decanol-1 (1:6275) with PCl_5 in CCl_4 see (1); with $SOCl_2$ + pyridine (80% yield (5)) or $SOCl_2$ without pyridine (91% yield (7)) see (5) (7); for prepn. from *n*-heptyl MgBr + γ-chloro-*n*-propyl *p*-toluenesulfonate see (4).]

C̄ htd. at 100° with aq. $Ba(OH)_2$ yields (2) decanol-1 (1:6275).

C̄ with Mg in dry ether contg. trace of I_2 gives (96% yield in 9 hrs. (8)) RMgCl.

3:8785 [illegible] (2) Schultz, *Ber.* **42**, 3610–3611 [illegible] nder, Marvel, *J. Am. Chem. Soc.* [illegible] '69 (1933). (6) Rothstein, *Bull.* [illegible] 38, 641. (8) Houben, Boedler, [illegible]

[For prepn. (80% yield (1)) from undecanol-1 (1:5890) + $SOCl_2$ + pyridine see (1), or with $SOCl_2$ alone (89% yield) see (2).]

No other data on $\bar{C}$ are recorded.

3:8803 (1) Rothstein, *Bull. soc. chim.* (5) **2**, 84 (1935). (2) Vogel, *J. Chem. Soc.* **1943**, 638, 641.

3:8805 1,8-DICHLORO-OCTANE (Octamethylene dichloride)

$C_8H_{16}Cl_2$ Beil. I-160, I_1—, I_2—

Cl.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.Cl

B.P. 240–242° (1)

[For formn. of $\bar{C}$ from octamethylenediamine [Beil. IV-271] with NOCl see (1); from 1,8-diphenoxyoctane (see below) with fumg. HCl see (1).]

$\bar{C}$ htd. with sodium phenolate yields (1) (2) 1,8-diphenoxyoctane [Beil. VI-148; VI_1-(85)], colorless tbls., m.p. 83.5–84°, sol. in hot alc., in ether, or in C_6H_6; not volatile with steam. [This prod. splits with HCl to yield (1) $\bar{C}$; with HBr to yield (1) 1,8-dibromooctane [Beil. I-160], m p. 15–16°, b.p. 270–272° sl. dec., b.p. 150–161° at 20–25 mm. (1).]

$\bar{C}$ refluxed with NaI in acetone for 4 hrs., solvent evaporated, ether-sol. portion of residual oil htd. for 4 hrs., with thiourea in isoamyl alc. gives (3) octamethylene *bis*-(ω,ω'-isothiourea hydrochloride), m.p. *185–186°* (3).

3:8805 (1) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 620, 623 (1898); *Cent.* **1899**, I 26. (2) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 822, 824 (1898); *Cent.* **1899**, I 254. (3) Kawai, Hosono, Shikinami, Yonechi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **16**, Nos. 306–309, 9–16 (1931); *Cent.* **1931**, II 1694; *C.A.* **25**, 5665 (1931).

3:8810 1-CHLORODODECANE (n-Dodecyl chloride; n-lauryl chloride)

$CH_3.(CH_2)_{10}.CH_2Cl$ $C_{12}H_{25}Cl$ Beil. I—, I_1—, I_2-(133)

B.P. 243–244° cor.	(1)	$D_4^{22} = 0.8673$ (3)	$n_D^{22} = 1.4421$ (3)
132–134° at 18 mm.	(2)	$D_4^{20} = 0.8673$ (9)	$n_D^{20} = 1.44255$ (9)
130° at 15 mm.	(3)		
125–126° at 10 mm.	(4)		
116.5° at 5 mm.	(9)		

[For prepn. (80% yield (3)) from dodecanol-1 (1:5900) + $SOCl_2$ + pyridine see (3); or with $SOCl_2$ in absence of pyridine (84% yield) see (9).]

$\bar{C}$ in alc. refluxed with thiourea for 4 days gives (5) *S-n*-dodecylisothiourea hydrochloride, m.p. 132–135° (5).

[For reactn. of $\bar{C}$ with liq. NH_3 see (6) (7); with various amines see (7).]

[For reactn. of $\bar{C}$ with KI see (1); for reactn. with Mg + ether see (2); for reaction of $\bar{C}$ with Li, Na, or K followed by CO_2 see (10).]

$\bar{C}$ htd. with pyridine in s.t. at 110° for 15 hrs. yields (8) *n*-dodecylpyridinium chloride, cryst. from alc. + ether or from C_6H_6 as monohydrate, m.p. 92° (8). [This quat. salt yields (8) on cat. hydrogenation *N*-(*n*-dodecyl)piperidinium hydrochloride, m.p. 188–189° (8).]

—*n*-Dodecyl mercuric chloride ($C_{12}H_{25}HgCl$): m.p. 114.0–114.5° (10). [Prepd. indirectly (10).]

3:8810 (1) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 485 (1925). (2) Oldham, Ubbelohde, *J. Chem. Soc.* **1938**, 204. (3) Rothstein, *Bull. soc. chim.* (5) **2**, 84 (1935). (4) Reed, Tartar, *J. Am.*

3:8800 n-DECANOYL CHLORIDE $CH_3.(CH_2)_8\,C{=}O$ (Cl) $C_{10}H_{19}OCl$ Beil. II - 356
(*n*-Caprinyl chloride) II_1—
II_2—

B.P. 232.3°	at 760 mm. (1)	F.P. −34.5° (1)
120°	at 20 mm. (2)	
114°	at 15 mm. (3)	
111–112°	at 14 mm. (4)	
104–105°	at 9 mm. (5)	
105–107°	at 8–9 mm. (6)	

Care must be taken not to confuse $\bar{C}$, the acid chloride of *n*-capric acid, with the corresponding relatives of *n*-caprylic acid (C_8) and of *n*-caproic acid (C_6); for this reason the name *n*-decanoyl chloride is preferred.

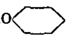
[For prepn. of $\bar{C}$ from *n*-decanoic acid (*n*-decylic acid) (*n*-capric acid) (1:0585) with PCl_5 (3), with PCl_3 (70% yield (1)), with $POCl_3$ (7), with oxalyl (di)chloride (3:5060) (5), or with $SOCl_2$ (6) (94% yield (4)) see indic. refs.]

[For use of $\bar{C}$ in prepn. of corresp. cellulose esters see (8) (9); for use in syntheses of various glycerides see (5) (6); for use in prepn. of derivs. of vanillylamine see (2) (10), for cat. hydrogenation to *n*-decylaldehyde (1:0222) see (11).]

$\bar{C}$ on hydrolysis (or even slowly in moist air) yields *n*-decanoic acid (1:0585) q.v. (for the amide, anilide, *p*-toluidide, and other derivatives corresponding to $\bar{C}$ see 1:0585).

3:8800 (1) Deffett, *Bull soc. chim Belg* **40**, 389–391 (1931). (2) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 856 (1934) (3) Krafft, Koenig, *Ber* **23**, 2385 (1890). (4) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86–89 (1939) (5) Averill, Roche, King, *J Am. Chem Soc* **51**, 868 (1929). [illegible] 705–710 (1932). (7) Grimm, *Ann* **157**, 272– [illegible] **1923**, IV 961. (9) Brit. 313,616, Aug 8, [illegible] *Soc.* **42**, 2125 (1919). [illegible] 39).

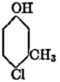
— **PHENYL CHLOROACETATE** $C_8H_7O_2Cl$ Beil. VI - 153
VI_1-(87)
VI_2-(154)

Cl.CH₂.CO.O

B.P. 230–235°	M.P. 45°	$D_4^{44} = 1.2202$	$n_D^{44} = 1.5146$

See 3:0565 *Division A: Solids.*

— **4-CHLORO-3-METHYLPHENOL** C_7H_7OCl Beil. VI - 381
VI_1-(187)
VI_2-(355)



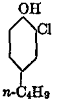
B.P. 235°	M.P. 57°

See 3:1535. *Division A: Solids.*

3:8803 1-CHLOROUNDECANE $CH_3.(CH_2)_9\,CH_2Cl$ $C_{11}H_{23}Cl$ Beil. S.N. 10
(*n*-Undecyl chloride;
1-chlorohendecane)

B.P. 240–241° at 772 mm. (2)		$D_4^{21.5} = 0.8570$ (1)	$n_D^{21.5} = 1.4350$ (1)
117° at 16 mm. (1)		$D_4^{20} = 0.8677$ (2)	$n_D^{20} = 1.44003$ (2)

3:8830 2-CHLORO-4-*n*-BUTYLPHENOL $C_{10}H_{13}OCl$ **Beil. S.N. 530-a**



B.P. 247–248° at 760 mm. (1) (4)
243–244° at 735 mm. (2)
110–115° at 3 mm. (3) (4)

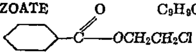
[For prepn. of C̄ from *p*-*n*-butylphenol (1:1771) by chlorination with Cl_2 (3), SO_2Cl_2 (4) (5); or $ClSO_3H$ (5) see indic. refs.; for prepn. of C̄ from *o*-chlorophenyl propionate by rearr. with $AlCl_3$ in nitrobenzene to *n*-propyl 3-chloro-4-hydroxyphenyl ketone and subsequent reductn. to C̄ see (4) (1).]

[For studies of bactericidal characteristics of C̄ see (1) (2) (6).]

C̄ with *α*-naphthoyl chloride (3:6930) *yields* (2) *4-n-butyl-2-chlorophenyl α-naphthoate*, m.p. 44–46° (2).

3:8830 (1) Klarmann, Shternov, Gates, *J. Am. Chem. Soc.* **55**, 2576–2589 (1933). (2) Blicke, Stockhaus, *J. Am. Pharm. Assoc.* **22**, 1090–1092 (1933); *Cent.* **1934**, I 1642; *C.A.* **28**, 4839 (1934). (3) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,010,595, Aug 6, 1935; *Cent.* **1936**, I 810; *C.A.* **29**, 6608 (1935). (4) Klarmann (to Lehn & Fink Products Corp.), U.S. 2,139,550, Dec. 6, 1938; *Cent.* **1939**, I 1807; *C.A.* **33**, 2285 (1939). (5) Blicke (to Regents of Univ. of Michigan), U S 1,980,966, Nov. 13, 1934; *Cent.* **1935**, I 3312; *C.A.* **29**, 476 (1935). (6) Klarmann, Shternov, Gates, *J. Lab. Clin. Med.* **20**, 40–47 (1934).

3:8860 *β*-CHLOROETHYL BENZOATE $C_9H_9O_2Cl$ **Beil. IX-112**
IX_1—



B.P. 255–257° at 762 mm. (1)
256–257° at 752 mm. (2)
254–255° at 749 mm. (3)
138.8° at 18 mm. (1)
125–130° at 14 mm. (4)
120–122° at 5 mm. (5)
118–120° at 2 mm. (6)

Oil, insol. aq.; eas. sol. alc, ether.

[For prepn. of C̄ from ethylene chlorohydrin (3:5552) with BzCl (3:6240) on htg. (yields: 90% (1), 84.5% (6), 55% (2)) (5) see indic. refs.; from ethylene glycol (1:6465) with benzoic acid (1:0715) at 100° in pres. of HCl gas (7); from ethylene oxide (1:6105) with BzCl (3:6240) at 190° (8); from 1,4-dioxane (1:6400) with BzCl (3:6240) + $TiCl_4$ (2 moles) at 150–180° for 10 hrs. (70% yield (9)); from ethylene + BzOH (1:0715) + Cl_2 + cat. as directed (10) see indic. refs.]

[For formn. of C̄ from *β*-chloroethyl iminobenzoate on warming (3), from *β*-chloroethyl *p*-toluenesulfonate with $C_6H_5COOMgBr$ (5% yield (11)), or from *bis*-(*β*-chloroethyl) sulfate with NaOBz at 170° (61.5% yield (4)) see indic. refs]

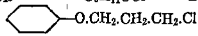
C̄ on htg. either alone or with $SnCl_4$ at 180–200° for 25 hrs. gives (9) ethylene glycol dibenzoate, m.p. 73°.

[C̄ on a mononitration is claimed (1) to yield mainly *β*-chloroethyl *m*-nitrobenzoate, but this alleged prod. is not described either in the article or elsewhere in the literature.]

C̄ with NaI (2 moles) in 90% alc. refluxed 6 hrs. gives (80% yield (1)) *β*-iodoethyl benzoate, b.p. 161–163° at 17 mm. (1).

Chem. Soc. **57**, 571 (1935). (5) Sprague, Johnson, *J. Am Chem. Soc.* **59**, 1838–1839 (1937). (6) Wibaut, Heiermann, Wagtendonk, *Rec. trav. chim.* **57**, 456–458 (1938). (7) Westphal, Jerchel, *Ber.* **73**, 1004–1011 (1940). (8) Karrer, Kahnt, Epstein, Jaffé, Ishil, *Helv Chim. Acta* **21**, 233–234 (1938). (9) Vogel, *J. Chem. Soc.* **1943**, 638, 641. (10) Meals, *J. Org. Chem.* **9**, 211–218 (1944).

3:8820 γ-PHENOXY-*n*-PROPYL CHLORIDE $C_9H_{11}OCl$ **Beil. VI-142**
(γ-Chloro-*n*-propyl phenyl ether) VI₁—



B.P.		M.P.	
245–255°	(1)	**11.8–12°** (1)	D_-^{20} = **1.1167** (4)
238–240° at 745 mm.	(2)		
139° at 25 mm.	(3)		

Colorless oil gradually turning yellowish in light.

[For prepn. of C̄ from γ-phenoxy-*n*-propyl alcohol (trimethylene glycol monophenyl ether) [Beil VI-147, VI_1-(85)] with $SOCl_2$ + pyridine (88% yield) see (3).]

[For prepn. of C̄ from 1-bromo-3-chloropropane (trimethylene glycol chlorobromide) (5) with potassium phenolate (1) or with alc. sodium phenolate (yields: 68% (6) (4), 55% (2)) see indic refs.; note that by this method some trimethylene glycol diphenyl ether (1,3-diphenoxypropane) (1:7170), m.p. 61°, b.p. 338–340° cor., may also be formed.]

[C̄ with diethyl sodiomalonate in usual way gives (yields: 77% (2), 56% (6), 55% (4)) diethyl (γ-phenoxy-*n*-propyl)malonate [Beil. VI-168], b.p. 271° dec. at 140 mm. (4), 265–266° at 140 mm. (7), 216–219° at 20 mm. (6), m p. 32° (7), 30° (4). — For analogous behavior of C̄ with diethyl sodio-methylmalonate see (7).]

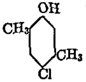
[C̄ with Na in ether undergoes a complex decomposition giving (8) cf. (7) sodium phenolate, propylene, cyclopropane, hexamethylene glycol diphenyl ether, etc]

[For study of rate of reactn. of C̄ with KI in acetone at 50° and at 60° see (3).]

—— *N*-(γ-Phenoxypropyl)phthalimide (phenyl γ-(phthalimido)-*n*-propyl ether) [Beil. XXI-472] ndls. from alc., m. p. 91° (9), 88° (10). [Not reported from C̄ but obtd. in 80% yield (10) from γ-phenoxy-*n*-propyl*bromide* with K phthalimide; also indirectly (9).]

3:8820 (1) Henry, *Bull. soc. chim.* (3) **15**, 1224 (1896). (2) Gabriel, *Ber.* **25**, 416–418 (1892). (3) Kirner, *J. Am Chem. Soc.* **48**, 2748–2749 (1926). (4) Granger, *Ber.* **28**, 1198–1200 (1895). (5) Allen, *Org* [illegible] 2
(1932); 8, 53, [illegible]
2570 (1893). [illegible]).
(9) Manske, *J* [illegible]

—— **4-CHLORO-3,5-DIMETHYLPHENOL** C_8H_9OCl **Beil. VI —**
VI₁—
VI₂-(463)



B.P. 246° **M.P. 115°**

See **3**:3505. *Division A: Solids.*

Cryst. (from abs. alc.) with agreeable musk-like odor.

[For prepn. of C̄ from 2,7-dimethyloctanediol-2,7 [Beil. I_1-(257)] with conc. HCl in the cold or with HCl gas in toluene see (1).]

3:0840 (1) Bouvet, *Bull. soc. chim.* (4) **17**, 204 (1915).

3:0843 CHLORAL *n*-BUTYLALCOHOLATE $C_6H_{11}O_2Cl_3$ Beil. I - 622
(Trichloroacetaldehyde *n*-butylhemiacetal) I_1— I_2—

$$Cl_3C{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}O{-}CH_2.CH_2.CH_2.CH_3$$

M.P. 49–50° (1) **B.P. 129–130° at 742 mm. (3)**
49° (2) (3) **129–130° cor. (1)**

Colorless ndls.

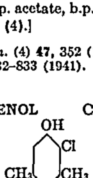
[For prepn. of C̄ from anhydrous chloral (3:5210) with 1 mole *n*-butyl alcohol (1:6180) (1) (2), or from chloral hydrate (3:1270) under reflux with *n*-BuOH (yields: 54% in 45 min., 28% in 60 min. (3)) or with tri-*n*-butyl orthoformate, see indic. refs.; for study of formn. of C̄ from chloral ethylalcoholate (3:0860) or from chloral *n*-propyl-hemiacetal by reflux with *n*-BuOH for 45 min. (yield 40–50%) see (3).]

[C̄ with AcCl gives (78% yield (1)) corresp. acetate, b.p. 129–131° at 20 mm. (1).]

[For behavior of C̄ with diazomethane see (4).]

3:0843 (1) Fourneau, Florence, *Bull. soc. chim.* (4) **47**, 352 (1930). (2) Kuntze, *Arch. Pharm.* **246**, 98 (1908). (3) Post, *J. Org. Chem.* **6**, 832–833 (1941). (4) Meerwein, Bersin, Burneleit, *Ber.* **62**, 1009 (1929).

3:0844 2-CHLORO-3,5-DIMETHYLPHENOL C_8H_9OCl Beil. VI —
(6-Chloro-*m*-5-xylenol) VI_1— VI_2- (464)



M.P. 49–50° (1)

[For formn. of C̄ from 3,5-dimethylphenol (*sym.-m*-xylenol) (1:1455) with SO_2Cl_2 in $CHCl_3$ (as by-product of the principal isomer 4-chloro-3,5-dimethylphenol (3:3505)) see (1).]

—— **2-Chloro-3,5-dimethylphenyl acetate:** unreported.
—— **2-Chloro-3,5-dimethylphenyl benzoate:** unreported.

3:0844 (1) Lesser, Gad, *Ber.* **56**, 974 (1923).

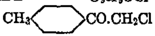
3:0846 1,1,1-TRICHLOROPROPANOL-2 $C_3H_5OCl_3$ Beil. I - 365
(β,β,β-Trichloroisopropyl alcohol; "Isopral") I_1-(185) I_2-(385)

$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CCl_3$$

M.P. 50–51°	**(1)**	**B.P. 161.8° cor.**	**at 774 mm.**	**(5)**
50°	**(2) (3)**	**161.8°**	**at 773 mm.**	**(1)**
49.2°	**(4) (6)**	**63–65°**	**at 20 mm.**	**(19)**
49°	**(5)**	**53–55°**	**at 12 mm.**	**(3)**
46–49°	**(19)**			

Hexag. cryst. from aq. (7); for crystallographic data see (2). — Spar. sol. aq., eas. sol. org. solvents (for data see (7)). — C̄ has high vapor press. (for measurement see (2)) and sublimes even at ord. temp. (for study of sublimation of C̄ by various methods see (5)).

—— *p*-METHYLPHENACYL CHLORIDE C_9H_9OCl Beil. VII - 309



VII_1-(165)

B.P. 260–263° M.P. 57–58°

See 3:1130. *Division A: Solids.*

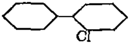
—— 2-CHLOROHYDROQUINONE $C_6H_5O_2Cl$ Beil. VI - 849

VI_1-(417)
VI_2 (844)

B.P. 263° M.P. 106°

See 3:3130. *Division A: Solids.*

—— 2-CHLOROBIPHENYL $C_{12}H_9Cl$ Beil. V - 579

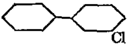


V_1-(272)
V_2-(483)

B.P. 274° at 738 mm. M.P. 34°

See 3:0300. *Division A: Solids.*

3:8940 3-CHLOROBIPHENYL $C_{12}H_9Cl$ Beil. V - 579
(3-Chloroxenene (1))



V_1—
V_2-(483)

B.P. 284–285° (2) (6) M.P. +16° (4)
150–160° at 6 mm. (3)
87° at 0.15 mm. (4)

Pale yel. oil. — By soln. in 2 vols. 96% alc., cooling to −18°, and scratching, C̄ has been obtd. in colorless cryst. from. (4).

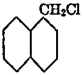
[For prepn. (27% yield (2), 16% yield (4), 13–25% yield (3)) from diazotized *m*-chloroaniline + C_6H_6 see (3) (4) (2).]

C̄ on oxidn. with CrO_3 in AcOH + V_2O_5 yields (5) *m*-chlorobenzoic acid (3:4392), m.p. 154°.

C̄ on nitration (no details (6)) gives a dinitro compd., 3-chloro-4,4′-dinitrobiphenyl, wooly flocks from alc., m.p. 202–203° (6) (9). [No other dinitro-3-chlorobiphenyls are recorded; of the possible mononitro-3-chlorobiphenyls only two (both prepd. indirectly) are known, viz., 4-nitro-3-chlorobiphenyl, m.p. 78.5–79.5° (7), and 3′-nitro-3-chlorobiphenyl, m.p. 101° (8).]

3:8940 (1) Hale, *J. Am. Chem. Soc.* **54**, 4458–4459 (1932). (2), Gomberg, Bachmann, *J. Am. Chem. Soc.* **46**, 2343 (1924). (3) Elks, Haworth, Hey, *J. Chem. Soc.* **1940**, 1285 (4) Weissberger, Sängewald, *Z. physik. Chem.* **B-20**, 154 (1933). (5) Bellavita, *Gazz. chim. ital.* **65**, 639 (1935). (6) Mascarelli, Gatti, *Gazz. chim. ital.* **63**, 660 (1933). (7) Schoepfle, Truesdale, *J. Am. Chem. Soc.* **59**, 376 (1937). (8) Mascarelli, Gatti, *Atti accad. sci. Torino*, **65**, 143–147; *Cent.* **1930**, II 1861. (9) Case, *J. Am. Chem. Soc.* **67**, 116, 118 (1945).

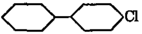
— 1-(CHLOROMETHYL)NAPHTHALENE $C_{11}H_9Cl$ Beil. V - 566
V_1—
V_2-(461)



B.P. 291–292° M.P. 32°

See 3:0250. *Division A: Solids.*

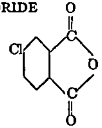
— 4-CHLOROBIPHENYL $C_{12}H_9Cl$ Beil. V - 579
V_1—
V_2-(483)



B.P. 291° at 745 mm. M.P. 77°

See 3:1912. *Division A: Solids.*

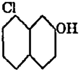
— 4-CHLOROPHTHALIC ANHYDRIDE $C_8H_3O_3Cl$ Beil. XVII - 483
$XVII_1$-(253)



B.P. 294.5° cor. at 720 mm. M.P. 98°

See 3:2725. *Division A: Solids*

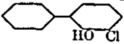
— 8-CHLORONAPHTHOL-2 $C_{10}H_7OCl$ Beil. VI - 649
VI_1—
VI_2-(604)



B.P. 307–308° M.P. 101°

See 3:2965. *Division A: Solids.*

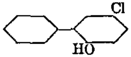
— 6-CHLORO-2-PHENYLPHENOL $C_{12}H_9OCl$ Beil. S.N. 539



B.P. 312° at 745 mm. M.P. 71–72°

See 3:1757. *Division A: Solids.*

3:8980 4-CHLORO-2-PHENYLPHENOL $C_{12}H_9OCl$ **Beil. S.N. 539**
(5-Chloro-2-hydroxybiphenyl)



B.P. 319°	**at 745 mm.**	**(1)**
178°	**at 15 mm.**	**(1)**
166–171° at	**10 mm.**	**(2)**
128–130° at	**2 mm.**	**(3)**

M.P. +11° (1) (4)

[*See also 6-chloro-2-phenylphenol* (3:1757).]

Important Note: Through the year 1944 (and perhaps in some cases beyond) the chlorophenyl-phenol of m.p. + 11° ($\bar{C}$) was regarded as having the structure 6-chloro-2-phenylphenol = 3-chloro-2-hydroxybiphenyl. In 1945, however, this view was corrected by the paper of Weissberger and Salminen (3); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting references prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of $\bar{C}$ from 2-hydroxybiphenyl (1:1440) with Cl_2 (note that 6-chloro-2-phenylphenol (3:1757) is also formed) see (1) (4) (3), for prepn. of $\bar{C}$ from 5-amino-2-hydroxybiphenyl (5) by diazotization and use of Cu_2Cl_2 reaction (27% yield (3)) see indic. refs.]

$\bar{C}$ is sol. in aq. 25% NaOH at 60° but on cooling seps. $Na\bar{A}.4H_2O$, m.p. 84–85° (1); anhydrous $Na\bar{A}$, m.p. 280° (1) (4) (for use in sepn. of $\bar{C}$ from the isomeric 6-chloro-2-phenylphenol (3:1757) see (1)). [For formn. of $Na\bar{A}$ in org. solvents such as MeOH, ether, or toluene see (8).]

The calcium salt of $\bar{C}$ is more sol. in aq. than the corresp. deriv. of the isomeric 6-chloro-2-phenylphenol (3:1757) (use in sepn. (2)).

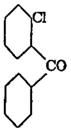
$\bar{C}$ on mononitration with HNO_3 in AcOH at 15–20° as directed gives (48% yield (3)) 5-chloro-2-hydroxy-3-nitrobiphenyl, yellow ndls., m.p. 57–58° (3).

[$\bar{C}$ on condensation with formaldehyde + morpholine yields (6) a prod. m.p. 125–126° (6).]

—— **4-Chloro-2-phenylphenyl benzoate:** m.p. 86–87° (7). [Note that this prod. does *not* distinguish $\bar{C}$ from the isomeric 6-chloro-2-phenylphenol (3:1757) whose benzoate has m.p. 88.5°.]

3:8980 (1) Britton, Bryner (to Dow Chem. Co.), U.S. 1,921,727; Aug 8, 1933; *Cent.* **1934**, I 128–129; *C.A.* **27**, 5086 (1933); Brit. 396,251, Aug 24, 1933; *Cent* **1934**, I 128–129; *C.A.* **28**, 578 (1934). (2) Rittler, Heller (to Chem. Fabrik von Heyden), Ger. 615,133, June 27, 1935; *Cent.* **1936**, I 884; *C.A.* **29**, 6347 (1935). (3) Weissberger, Salminen, *J. Am. Chem. Soc.* **67**, 58–60 (1945). (4) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug. 14, 1934; *C.A.* **28**, 6160 (1934). (5) Vorozhtsov, Troshchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 431–437 (1938); *Cent.* **1940**, II 2152; *C.A.* **32**, 7907 (1938). (6) Bruson (to Röhm and Haas Co.), U.S. 2,040,039, May 5, 1936; *Cent.* **1936**, II 1386–1387; *C.A.* **30**, 4177 (1936). (7) Harris, Christiansen, *J. Am. Pharm. Assoc.* **24**, 553–557 (1935). (8) Mills (to Dow Chem. Co.), U.S. 1,955,080, April 17, 1934; *Cent.* **1934**, II 1991; *C.A.* **28**, 3743 (1934).

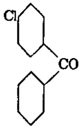
— 2-CHLOROBENZOPHENONE $C_{13}H_9OCl$ Beil. VII - 419
VII₁-(227)



B.P. 330° cor. M.P. 45–46°

See 3:0715. *Division A: Solids.*

— 4-CHLOROBENZOPHENONE $C_{13}H_9OCl$ Beil. VII - 419
VII₁-(227)



B.P. 332° at 771 mm. M.P. 77–78°

See 3:1914. *Division A: Solids.*

CHAPTER XX

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9000–3:9299 (C_3–C_6 inclusive)

(Arranged in sequence of empirical formulas)

3:9030 MALONYL DICHLORIDE $O{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}O$ $C_3H_2O_2Cl_2$ Beil. II - 582
II_1-(252)
II_2-(529)

B.P. 58°	at 27 mm. (1) (2) (3)	$D_4^{22.9} = 1.4505$ (4)	$n_D^{23.4} = 1.45973$ (4)
58°	at 26 mm. (4)		
53.6°	at 22 mm. (5)	$D_4^{20} = 1.4509$ (5)	
53–54°	at 19 mm. (4)	1.450 (4)	$n_D^{20} = 1.4639$ (5)
55°	at 15 mm. (6)		
47°	at 15 mm. (7)	$D_4^{18.6} = 1.4486$ (4)	$n_D^{18.4} = 1.46205$ (4)
47°	at 13 mm. (4)		

Colorless liq. turning dark red on stdg. (6).

[For prepn. of $\bar{C}$ from malonic acid (1:0480) with $SOCl_2$ (yield 70% (8), 60% (6), 50% (9)) (1) (2) or with PCl_5 (yield: 68% (3), 36% (7)) see indic. refs.; for formn. of $\bar{C}$ from carbon suboxide with dry HCl gas see (10); for mfg. of $\bar{C}$ from methylene dichloride (3:5020) with CO, COS, or $COCl_2$ (3:5000) + cat. at 700° see (11).]

[$\bar{C}$ in ether or EtOAc with Ag_2O, PbO, ZnO, etc., yields (8) carbon suboxide, b.p. +7°; $\bar{C}$ treated at 0° with dry HBr gas yields (12) malonyl dibromide, b.p. 55–57° at 11 mm. (12); $\bar{C}$ on cat. hydrogenation as specified (13) yields a condensation prod., m.p. 83°, of formylglutaconic acid.]

[$\bar{C}$ with acetone + $CaCO_3$ yields (14) mainly $CH_3.CO.CH_2.CO.CH_2.CO.Cl$ [Beil. III_1-(263)] + a little phloroglucinol (1:1620) (the acid chloride itself, however, is quant. conv. to phloroglucinol by further htg. with $CaCO_3$).]

[$\bar{C}$ with $AlCl_3$ + C_6H_6 yields (1) dibenzoylmethane (1:1480), m.p. 78°; for reactn. of $\bar{C}$ with $AlCl_3$ + naphthalene (1:7200) yielding (15) (16) *peri*-naphthindandione (1,8-malonylnaphthalene) [Beil. VII_1-(391)] see indic. refs.; for reactn. of $\bar{C}$ with acenaphthene (1:7225) yielding (15) (17) *peri*-acenaphtheneindandione (5,6-malonylacenaphthene) which on oxidn. gives (17) (18) naphthalene-1,4,5,8-tetracarboxylic acid [Beil. IX-1002, [illegible] .V-272], [illegible] l is no longer evolved gives (85% yield (19)) malonyl-diurethane, cryst. from alc., m.p. 124° (19).

$\bar{C}$ on hydrolysis with aq. yields malonic acid (1:0480). [Note that the half acid chloride of malonic acid has m.p. 65° dec. (20).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{C}$ see malonic acid (1:0480).

3:9030 (1) Auger, *Ann. chim.* (6) **22**, 347–350 (1891). (2) Asher, *Ber.* **30**, 1023–1024 (1897). (3) Clark, Bell. *Trans. Roy. Soc. Can.* (3), **27**, III 97–107 (1933). (4) von Auwers, Schmidt, *Ber.* **46**, 477–478 (1913). (5) Martin, Partington, *J. Chem. Soc.* **1936**, 1181. (6) McMaster, Ahmann, *J. Am. Chem. Soc.* **50**, 146 (1928). (7) Black, Shaw, Walker, *J. Chem. Soc.* **1931**, 276. (8) Staudinger, Bauer, *Ber.* **41**, 4163–4465 (1908). (9) Nightingale, Alexander, *J. Am. Chem. Soc*
r. **39**, 696 (1906).
Oil Development Co), U.S. 2,062,344, Dec. 1, 1936;
(12) Fleischer, Hittle, Wolff, *Ber.* **53**, 1848 (1920).
(13) Fröschl, Maier, *Monatsh.* **59**, 261, 269–270 (1932). (14) Komninos, *Compt. rend.* **167**, 781 (1918); *Bull. soc. chim.* (4) **23**, 452–455 (1918). (15) Fleischer, Retze, *Ber.* **55**, 3282, 3285 (1922). (16) Badische Anilin und Soda Fabrik, Ger. 283,365, Apr 10, 1915; *Cent.* **1915**, I 965. (17) Eckert (to I.G.), Ger. 439,511, Jan 14, 1927, *Cent.* **1927**, I 1527. (18) Eckert (to Grasselli Dyestuffs Corp.), U.S. 1,612,103, Dec 28, 1926; *Cent.* **1927**, I 1527, *C.A.* **21**, 593 (1927). (19) Basterfield, Woods, Whelen, *J. Am. Chem. Soc.* **49**, 2945 (1927). (20) Staudinger, Ott, *Ber.* **41**, 2211–2212 (1908).

3:9031 α-CHLOROACROLEIN (2-Chloropropen-2-al-1) $CH_2{=}C(Cl){-}CHO$ C_3H_3OCl Beil. I — I_1— I_2-(785)

B.P. 40° at 30 mm. (1)	$D^{20}_{-} = 1.199$ **(2) (3)**	$n^{20}_{D} = 1.463$ **(2) (3)**
39–40° at 30 mm. (2)	$D^{15}_{-} = 1.205$ **(3)**	
29–31° at 17 mm. (3)	$D^{0}_{-} = 1.272$ **(3)**	

Colorless strongly lachrymatory liq. with pronounced irritating effect on mucous membranes.

[For prepn. of $\bar{C}$ from acrolein (1:0115) in aq. with Cl_2 (50% yield (2)) or from α,β-dichloropropionaldehyde (3:9034) by loss of 1 HCl with hot aq. NaOAc (27% yield (3)) (1) see indic. refs.]

$\bar{C}$ readily polymerizes.

[$\bar{C}$ in CCl_4 with Cl_2 in cold adds 1 mole halogen giving (2) α,α,β-trichloropropionaldehyde (3:9033).]

[$\bar{C}$ in dry ether with Br_2 in cold adds 1 mole halogen giving (2) α-chloro-α,β-dibromopropionaldehyde, b.p. 105° at 55 mm., $D^{20}_{-} = 2.17$, $n^{20}_{D} = 1.548$.]

[For conversion of $\bar{C}$ with EtOH to α-chloroacrolein diethylacetal, b.p. 158–160°, see (4).]

3:9031 (1) Muskat, Becker, *J. Am. Chem. Soc* **52**, 816–817 (1930). (2) Berlande, *Bull. soc. chim.* (4) **37**, 1392–1393 (1925). (3) Moureu, Robin, Boisemenu, *Ann. chim.* (9) **15**, 210–211 (1921). (4) The Distillers Co., Ltd., Staudinger, Tuerck, Lichtenstein, Brit. 554,570, July 9, 1943; C.A. **39**, 312 (1945).

3:9032 *d,l*-α,β-DICHLOROPROPIONYL CHLORIDE $C_3H_3OCl_3$ Beil. S.N. 162

$CH_2Cl{-}CHCl{-}C({=}O)Cl$

B.P. 52–54° at 16 mm. (1)	$D^{20}_{4} = 1.4757$ **(2)**	$n^{20}_{D} = 1.47640$ **(2)**
43–44° at 10 mm. (2)		

[For prepn. of $\bar{C}$ from α,β-dichloropropionic acid (3:0855) with $SOCl_2$ see (1) (2); for formn. of $\bar{C}$ from glyceric acid (α,β-dihydroxypropionic acid) with PCl_5 see (4) (3) (5).]

[$\bar{C}$ with alcohols yields alkyl α,β-dichloropropionates; e g., cf. (1) (2) (3).]

$\bar{C}$ on hydrolysis yields α,β-dichloropropionic acid (3:0855) q.v.

3:9032 (1) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940). (2) Leimu, *Ber.* **70**, 1046, 1050 (1937). (3) Werigo, Werner, *Ann.* **170**, 163–167 (1874). (4) Werigo, Okulitch, *Ann.* **167**, 49 (1873). (5) Wichelhaus, *Ann.* **135**, 253 (1865); **143**, 3 (1867).

[$\bar{C}$ with hexanone-2 directly has not been studied, but $\bar{C}$ with *n*-butylacetylene (1:8055) in pres. of $Et_2O.BF_3$/HgO/MeOH/trichloroacetic acid gives (104) 4-(chloromethyl)-2-*n*-butyl-2-methyl-1,3-dioxolane, b.p. 109° at 25 mm.]

[$\bar{C}$ with acetophenone (1:5515) in pres. of H_2SO_4 or HCl gives (105) a prod. presumably 4-(chloromethyl)-2-methyl-2-phenyl-1,3-dioxolane, b.p. 153–153.3° at 40 mm., which with 2 *N* HCl at 60° is hydrolyzed into its original components.]

Behavior of $\bar{C}$ with Salts of Organic Acids

$\bar{C}$ reacts with salts of organic acids to give in general the corresp. glycerol α-esters.

With salts of aliphatic monobasic acids. [$\bar{C}$ with Na formate on htg is claimed to yield (106) (45) glycerol α-monoformate [Beil. II-24, II_1-(19), II_2-(33)], but owing to the instability of this prod. the reliability of its supposed constants has been questioned (8)]

[$\bar{C}$ with NaOAc or KOAc in s.t. at 150–160° yields (107) glyceryl α-acetate [Beil. II-146, II_1-(69), II_2-(159)], b.p. 129–131° at 3 mm., D_4^{20} = 1,2060, n_D^{20} = 1.4517 (108), but the reactn. is accompanied by some formn of glyceryl diacetate and glyceryl triacetate.]

[For corresp. reactions of $\bar{C}$ with sodium salts of *n*-butyric acid (1:1035), isobutyric acid (1:1030), *n*-valeric acid (1:1060), isovaleric acid (1:1050), and *n*-caproic acid (1:1130) see (8).]

[$\bar{C}$ with K laurate in s.t. at 180° under CO_2 (109) or $\bar{C}$ with Na laurate at 130° (110) gives glyceryl α-laurate ("α-monolaurin") [Beil. II-362, II_1-(157), II_2-(320)], m.p. 63° (111), cf. (112), 62° (2).]

[$\bar{C}$ with K myristate in s.t. at 180° under CO_2 (109), or $\bar{C}$ with sodium myristate at 110–115° for 8–10 hrs. (110), gives (70% yield (110)) glyceryl α-myristate ("α-monomyristin") [Beil. II-366, II_1-(162), II_2-(327)], m.p. 68° (109) (113), 67.3° (111) cf. (112).]

[$\bar{C}$ with K palmitate in s.t. at 180° under CO_2 (109), or $\bar{C}$ with Pb palmitate at 112° under CO_2 (113), gives (50% yield (113)) glyceryl α-palmitate ("α-monopalmitin") [Beil. II-373, II_2-(338)], m.p. 74–75° (2), 77° (111) cf. (112).]

[$\bar{C}$ with K stearate in s.t. at 180° under CO_2 (109), or $\bar{C}$ with sodium stearate at 110–115° for 8–10 hrs. (110) cf. (114), gives glyceryl α-stearate ("α-monostearin"), m.p. 81.1° (111) cf. (112).]

With salts of amino acids. [For analogous formn. of corresp. glyceryl mono esters from $\bar{C}$ with sodium salts of aminoacetic acid (glycine) (115), α-aminopropionic acid (alanine) (115), α-amino-isocaproic acid (leucine) (116) see indic. refs]

With alkali cyanides. [$\bar{C}$ in 95% alc. with aq. KCN (or NaCN) in s.t. at 100° for 36 hrs., followed by hydrolysis, gives (9) 28% yield of the lactone of β,γ-dihydroxy-*n*-butyric acid (β-hydroxy-*n*-butyro-γ-lactone), m.p. 22.5–26° (9), accompanied by (23% yield (9)) the lactone of γ-hydroxyisocrotonic acid, m.p. +5° (9) (presumably formed by loss of H_2O from the former).] Cf. behavior of "glycerol β-monochlorohydrin" (3:9039).

Behavior of $\bar{C}$ with Other Non-Nitrogenous Organic Reactants

With alkyl halides (or their equivalents). [$\bar{C}$ with MeI + silver oxide (15), or $\bar{C}$ with methyl *p*-toluenesulfonate at 150° for 5 hrs. (117), or $\bar{C}$ with diazomethane (118) gives the corresp. dimethyl ether, viz., 3-chloro-1,2-dimethoxypropane, b.p. 156–157° at 760 mm. (117), 156–158° (118), 156° (15), D_4^{25} = 1.08 (15), n_D^{25} = 1.43 (15).]

[Note that the corresp. diethyl ether, viz., 3-chloro-1,2-diethoxypropane, b.p. 69.8–70.4° at 14 mm., D_4^{19} = 1.026, n_D^{20} = 1.4246, has been prepd. indirectly (119).]

With RMgX cpds. [$\bar{C}$ with EtMgBr (2 moles) reacts in an obscure fashion yielding [illegible] 5455). — $\bar{C}$ with *iso*-AmMgBr (4 moles) (perhaps acting [illegible] es (25% yield (120)) 2,5-dimethylhexanediol-1,2 [Beil. [illegible], 129–132° at 11 mm.]

[C̄ with C_6H_5MgBr (4 moles) (perhaps acting through intermediate acetol) gives (120) (121) (60% yield (120)) 2-phenylpropanediol-1,2 [Beil. VI-930] accompanied by some 3-phenylpropanediol-1,2 [Beil. VI-929].]

Behavior of C̄ with Amines

With primary amines. *With aliphatic primary amines.* [C̄ with *n*-heptadecylamine (122) or its hydrochloride gives a prod. which may be the expected *N*-(β,γ-dihydroxy-*n*-propyl)*n*-heptadecylamine.]

With aromatic primary amines. [C̄ with aniline (2 moles) + a little aq. refluxed for 1 hr., then neutralized, gives (63% yield (124)) *N*-(β,γ-dihydroxy-*n*-propyl)aniline [Beil. XII-183], b p. 249–250° at 50 mm. (125), 200–203° (124), m p. 42° (124), 52° (125).]

[C̄ with *p*-aminophenol gives (126) *N*-(β,γ-dihydroxy-*n*-propyl)-*p*-aminophenol, m.p. 192°, used as photographic developer (127); for analogous reactions of C̄ with *p*-anisidine giving *N*-(β,γ-dihydroxy-*n*-propyl)-*p*-anisidine, m p. 75–76° see (126), or of C̄ with *p*-phenetidine giving *N*-(β,γ-dihydroxy-*n*-propyl)-*p*-phenetidine, m p 93° (126), 90–92° (128), see indic refs.]

With secondary amines. *With aliphatic secondary amines* [C̄ with Me_2NH + aq. NaOH at 20–40° (129) or C̄ with Me_2NH in s.t. at 100° for 5–6 hrs. (130) (131) cf. (132) gives 3-(dimethylamino)propanediol-1,2 [Beil. IV-302], b.p. 220° cor. at 749 mm. (130), 111° at 15 mm. (132) — C̄ with Et_2NH in s t. at 100° for 5–6 hrs. (131) cf. (130) (132) gives 3-(diethylamino)propanediol-1,2 [Beil. IV-302], b p. 233–235° at 748 mm (130) (131), 106° at 3 mm. (132) (corresp. *bis*-(*N*-phenylcarbamate), m p. 106 5° (133); corresp. *bis*-(*N*-phenylcarbamate)monohydrochloride, m.p. 109° (133)).]

With heterocyclic secondary amines [C̄ with piperidine in s t. at 100° for 4–5 hrs. (131, cf. (132) or in ord flask at 100° for 1½ hrs. (134) gives 3-(piperidino)propanediol-1,2 [Beil XX-34, XX_1-(12)], m p 83° (135) (132), 79–80° (136), 67–68° (134) (corresp. *bis*-(*p*-nitrobenzoate), m.p. 108° (135); corresp. *bis*-(*N*-phenylcarbamate)monohydrochloride ("Diothane"), m.p. 201–202° cor. (137), 197–198° u.c (?) (133)). — Note that in prepn. of "Diothane" the influence of the purity of the piperidine has been studied (137); that 3-(piperidino)propanediol-1,2 yields a *mono*-(*N*-phenylcarbamate)monohydrochloride, m.p. 176–177° (133); for resolution of *d,l*-3-(piperidino)propanediol-1,2 into its opt. act. enantiomorphs and prepn. of the corresp opt act. "Diothanes" see (138)]

With tertiary amines. [C̄ with Me_3N anhydrous (139) or in aq soln in s.t. at 100° for 8 hrs. (31) or in alc. soln. in s.t. at 100° for 6 hrs. (140) gives trimethyl-(β,γ-dihydroxy-*n*-propyl)-ammonium chloride [Beil. IV-302]. — C̄ with Et_3N in s.t. at 100° for 8 hrs. gives (141) triethyl-(β,γ-dihydroxy-*n*-propyl)-ammonium chloride [Beil. IV-303]. — For analogous behavior of C̄ with tri-*n*-propylamine, quinoline, and strychnine see (141). — For quat. salt from C̄ with *N,N*-dimethyl "stenyl" amine see (142).]

Behavior of C̄ with Other Nitrogenous Org. Reactants

[C̄ with diazomethane gives (118) the corresp. dimethyl ether for which see above under behavior of C̄ with alkyl halides.]

[C̄ with aq. Na_2NCN stood for 12 hrs., then shaken with benzoyl chloride, gives (143) the tribenzoate, m.p. 130° of 5-(hydroxymethyl)-2-aminooxazoline; substitution of benzenesulfonyl chloride for the benzoyl chloride yields (144) corresp. *tris*-(benzenesulfonate), m.p. 158°.] Cf. behavior of epichlorohydrin (3:5358).

—— **Glycerol α-monochlorohydrin α′-acetate (γ-chloro-β-hydroxy-*n*-propyl acetate):** b.p. 240° (see 3:6775).

—— Glycerol α-monochlorohydrin β-acetate (β-chloro-β'-hydroxy-isopropyl acetate): b.p. 218° (see 3:6517).

—— Glycerol α-monochlorohydrin α,β-diacetate: b.p. 245° (see 3:6840).

—— Glycerol α-monochlorohydrin α'-benzoate: unreported.

—— Glycerol α-monochlorohydrin β-benzoate: unreported.

—— Glycerol α-monochlorohydrin α',β-dibenzoate: unreported.

Ⓓ Glycerol α-monochlorohydrin di-(*p*-nitrobenzoate): m.p. 108–109° u.c. (14), 108° (15), 107–108° (2). [From $\bar{C}$ with *p*-nitrobenzoyl chloride (2 moles) in pyridine at room temp. for several days (93–96% yield (14)) or in $CHCl_3$ soln. with quinoline as acid acceptor (100% yield (2)); note that this prod. depresses m.p. (121–122°) of the corresp. deriv. of the isomeric glycerol β-monochlorohydrin (3:9039) (14).]

—— Glycerol α-monochlorohydrin α'-(?)-(*N*-phenylcarbamate): m.p. 128–129° (16), 127–129° (9), 126° (42). [From $\bar{C}$ with phenyl isocyanate in 7% yield (9); note that for the corresp. deriv. of glycerol β-monochlorohydrin (3:9039) the m.p. is 133–136°.]

Ⓓ *N*-(β,γ-dihydroxy-*n*-propyl)phthalimide: m.p. 111.5–112.5° (145), 111° (46). [From $\bar{C}$ with K phthalimide (100% yield (46)), but no details of conditions are stated.]

3:9038 (1) Fairbourne, Gibson, Stephens, *J. Soc. Chem. Ind.* **49**, 1021–1023 (1930). (2) Fair-

(1931). (10) Gibson, *J. Soc. Chem. Ind* **50**, 971 (1931).

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–452. (16) Rider, Hill,
17, 67–75 (1879). (18)
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(1931). (20) Sturgis (to General Explosives Co.), U.S. 1,473,685, Nov. 13, 1923, *Cent* **1924**, I 720; *C.A.* **18**, 472 (1924).

(21) Wrightsman (to du Pont Co), U.S 1,751,377, March 18, 1930; *Cent.* **1930**, II 2476; *C.A.* **24**, 2605 (1930): U.S. 1,891,255, Dec. 20, 1932; *Cent.* **1933**, I 1717; *C.A.* **27**, 2036 (1933). (22) Rosenthal (to F. Bayer & Co.), Ger. 406,426, Nov. 18, 1924; *Cent.* **1925**, I 908; not in *C.A.* (23) Schütz, *Cellulosechem.* **19**, 33–38 (1941); *C.A.* **36**, 5008 (1942). (24) I G., Brit. 474,677, Dec. 2, 1937; *Cent.* **1938**, I 2045, *C A.* **32**, 3064 (1938) · French 805,557, Nov. 24, 1936; *Cent.* **1937**, I 3397; *C.A.* **31**, 4417 (1937). (25) Cla
Cent. **1935**, I 2548; *C.A.* **29**, 11
Cooper, Forstner, *Biochem. J.*
(29) Conant, Quayle, *Org Synt*
(1932); **2**, 33–35 (1922). (30)
(1854).

(31) Hanriot, *Ann chim.* (5) **17**, 80, 100, 114 (1879). (32) Nivière, *Compt. rend.* **156**, 1628
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1920).
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1908).
; *C.A.*
6, 1660 (1912).

(41) Deutsche Sprengstoff, A.G., Ger. 229,872, Jan. 6, 1911; *Cent.* **1911**, I 358; *C.A.* **5**, 2557 (1911); Ger. 229,536, Dec. 22, 1910; *Cent.* **1911**, I 274; *C.A.* **5**, 2557 (1911); Ger. 201,230, Sept. 25, 1908; *Cent.* **1908**, II 1218; *C.A.* **3**, 377 (1910). (42) Carré, Mauclere, *Compt. rend.* **192**, 1568 (1931). (43) Brönsted, Mary Kilpatrick, Martin Kilpatrick, *J. Am. Chem. Soc.* **51**, 430–431, 445–446 (1929). (44) Fourneau, Ribas y Marques, *Bull. soc. chim.* (4) **39**, 700 (1926). (45) Delaby,

[For prepn. of $\bar{C}$ from 1,1,1-trichloropropanone-2 (3:5620) by reduction with fused $Al(OEt)_3$ in abs. alc. under H_2 or N_2 (8) or with $AlEt_3$ etherate in ether (3) (yields: 67% (8), 65% (3)) see indic. refs.; for prepn. of $\bar{C}$ from chloral (3:5210) with CH_3MgBr (9) (19) (2) cf. (4) or MeMgI (2) cf. (4) (yield: 40% (9) (2)) see indic refs. (note that by this method the normal *addn* of RMgX leading to $\bar{C}$ is accompanied by *reduction* leading to 2,2,2-trichloroethanol (3:5775) and the relative proportion of these two reactions is profoundly influenced by the pres. of metal salts (9)); for prepn of $\bar{C}$ from chloral (3:5210) with $ZnMe_2$ see (6).]

$\bar{C}$ is used as hypnotic pharmaceutical under the trade name "Isopral" (10), for use as seed disinfectant see (11); for study of disinfectant power and toxicity see (12); for comparative study of narcotic action see (13) — For study of tests for $\bar{C}$ see (7) (14).

$\bar{C}$ on reduction in aq. AcOH + Zn dust in cold yields (15) 1,1-dichloropropene-1 (3:5120).

$\bar{C}$ on oxidn. with fumg. HNO_3 under reflux for 5 hrs. gives (2) trichloroacetic acid (3:1150); use of $K_2CR_2O_7$ + H_2SO_4 gives only insignificant yields (2) while less strong HNO_3 even after 4 hrs. at 100° has only slight action (2).

$\bar{C}$ with P_2O_5 on htg loses H_2O giving (84% yield (19)) (2) 1,1,1-trichloropropene-2 (3:5345), b.p. 114–115° at 757 mm. (2).

[$\bar{C}$ with HNO_3/H_2SO_4 mixt. yields (2) β,β,β-trichloroisopropyl nitrate, oil, $D^{13}_{-} = 1.499$, $n_D^{-} = 1.47892$, but decompg. on htg — $\bar{C}$ with PCl_3 or PCl_5 yields (2) (1) various partial ester/acid chloride derivs. of phosphorous or phosphoric acids — $\bar{C}$ with $SOCl_2$ evolves HCl + SO_2 and also yields (2) a liq presumably β,β,β-trichloroisopropyl chlorosulfonate.]

$\bar{C}$ with aq or alc. NaOH or conc. aq Na_2CO_3 gives on htg. (16) (17) mainly acetaldehyde (1.0100) and lactic acid (1:0400), also accompanied by formic acid (1:1005) and carbon monoxide; for use of this reactn. in detection of $\bar{C}$ see (14) — $\bar{C}$ with EtOH/NaOEt on htg. gives (15) ethyl α-ethoxypropionate [Beil. III-280, III_1-(109), III_2-(206)], b p. 155° cor. at 760 mm, $D_4^{20} = 0.9446$, $n_D^{20} = 1.40125$.

[$\bar{C}$ with AcCl yields (2) β,β,β-trichloroisopropyl acetate, b.p. 180–181° cor. 766 mm., m p. + 8°, $D^{13}_{13} = 1.353$, $n_D^{-} = 1.46017$ (2).]

—— β,β,β-Trichloroisopropyl carbamate: cryst. from C_6H_6, m.p. 125° (18). Prepd. indirectly from β,β,β-trichloroisopropoxy MgBr with phosgene in toluene, followed by treatment with NH_3 (35% yield (18)).]

3:0846 (1) Henry, *Compt rend.* **138**, 205 (1904). (2) Vitoria, *Rec trav. chim.* **24**, 265–287 (1905); *Bull. acad. roy. Belg* **1904**, 1087–1123; *Cent* **1905**, I 344–345. (3) Meerwein, Hinz, Majert, Sonke, *J. prakt. Chem* (2) **147**, 236–237 (1936). (4) Bayer and Co, Ger. 151,545, May 20, 1904; *Cent.* **1904**, I 1586. (5) Eder, Haas, *Mikrochemie* (Emich Festschrift), **1930**, 59, 67, 78, 80. (6) Garzarolli-Thurnlackh, *Ann.* **210**, 77–79 (1881). (7) Genot, *J. pharm. Belg* **12**, 735–736 (1930); *Cent.* **1930**, II 3062. (8) Meerwein, Schmidt, *Ann* **444**, 234 (1925). (9) Kharasch, Kleiger, Martin, Mayo, *J. Am. Chem. Soc.* **63**, 2306–2307 (1941). (10) *Cent.* **1903**, II 899.

(11) von Leuthold, Austrian 145,527, May 11, 1936, *Cent.* **1936**, II 1052. (12) Howard, Stimpert, *J. Am. Pharm. Assoc* **14**, 487–489 (1925), *Cent* **1925**, II 1696, *C.A.* **19**, 2864 (1925). (13) Lendle, *Arch exptl. Path. Pharmakol.* **125**, 287–300 (1927), *Cent.* **1928**, I 715; *C.A.* **22**, 639 (1928). (14) Serantes, *Anales soc. quím. argentina* **12**, 199–200 (1924), *C.A.* **19**, 704 (1925). (15) Wohl, Roth, *Ber.* **40**, 215–216 (1907). (16) Hebert, *Bull. soc. chim.* (4) **27**, 49 (1920). (17) Mossler, *Monatsh.* **29**, 583–590 (1908). (18) Yoder, *J. Am. Chem. Soc.* **45**, 479 (1923). (19) Kharasch, Rossin, Fields, *J. Am. Chem. Soc.* **63**, 2559–2560 (1941).

wein, Hinz, *Ann.* **484**, 17–18 (1930). (119) Meerwein, Hinz, Hofmann, Kroning, Pfeil, *J. prakt. Chem.* (2) **147**, 278 (1936/7). (120) Grignard, *Compt. rend.* **141**, 45 (1905); *Ann. chim.* (8) **10**, 31–40 (1907)

(121) Grignard, Ger. 164,883, Nov. 16, 1905; *Cent.* **1905**, II 1751. (122) I.G., Brit, 358,114, Oct. 29, 1931; [illegible]
Cent. **1932**, I 1[illegible]
[*C.A.* **26**, 2288
Cent. **1935**, II [illegible]
(1894). (126) Kolshorn, Ger. 346,385, Dec. 29, 1921, Ger. 346,386, Jan. 2, 1922; [*Cent.* **1922**, II 574]; not in *C.A.*: Ger. 343,151, Oct. 28, 1921; [*Cent.* **1922**, II 143]; not in *C.A.*; Brit. 145,614, June 29, 1920; *C.A.* **14**, 3427 (1920); not in *Cent.*; Brit. 155,575/6, Jan. 13, 1921; *Cent.* **1921**, II 601; *C.A.* **15**, 1535 (1921): French 519,129, June 4, 1921; *Cent.* **1921**, IV 803; not in *C.A.* (127) Kolshorn, Ger. 343,994, Nov. 12, 1921; *Cent.* **1922**, II 604; not in *C.A.* (128) Bergmann, Ulpts, Camacho, *Ber.* **55**, 2807–2809 (1922). (129) Alquist, Slagh (to Dow Chem. Co.), U.S. 2,147,226, Feb. 14, 1939; *Cent.* **1939**, II 526; *C.A.* **33**, 3818 (1939). (130) L. Knorr, E. Knorr, *Ber.* **32**, 756–757 (1899).

(131) Roth, *Ber.* **15**, 1149–1153 (1882). (132) Rider, Hill, *J. Am. Chem. Soc.* **52**, 1528–1530 (1930). (133) Rider, *J. Am. Chem. Soc.* **52**, 2115–2118 (1930); U.S. 2,004,132, June 11, 1935; *Cent.* **1935**, II 3545; *C.A.* **29**, 4902 (1935). (134) Magidson, Strukow, *Arch. Pharm.* **271**, 576–577 (1933). (135) Einhorn, Fiedler, Ladisch, Uhlfelder, *Ann.* **371**, 158–161 (1910). (136) Pyman, *J. Chem. Soc.* **93**, 1795 (1908). (137) Rider, Cook, *J. Am. Chem Soc.* **59**, 1741 (1937). (138) Raasch, Brode, *J. Am. Chem. Soc.* **64**, 1112–1113 (1942). (139) Meyer, *Ber.* **2**, 186–188 (1869). (140) Schmidt, Hartmann, *Ann.* **337**, 102 (1904).

(141) Bienenthal, *Ber.* **33**, 3500–3506 (1900). (142) du Pont Co., Brit. 477,981, Feb. 10, 1938; *Cent.* **1938**, II 183; not in *C.A.* (143) Fromm, Pirk, *Ann.* **442**, 143–144 (1925). (144) Fromm, Kapeller-Adler, *Ann.* **467**, 253–254 (1928). (145) Gabriel, Ohle, *Ber.* **50**, 824 (1917). (146) Hatch, Alexander, *J. Am. Chem. Soc.* **67**, 688 (1945).

3:9039 2-CHLOROPROPANEDIOL-1,3 (Glycerol β-monochlorohydrin, "β-monochlorohydrin," β-chlorotrimethylene glycol, β,β′-dihydroxyisopropyl chloride)

$$\begin{array}{c} CH_2OH \\ | \\ H—C—Cl \\ | \\ CH_2OH \end{array}$$

$C_3H_7O_2Cl$

Beil. I - 476
I_1-(247)
I_2-(542)

B.P. [146°	at 18 mm.	(1) (2)]	D_4^{20} = 1.3219 (4) n_D^{20} = 1.4831 (4)
124.5–125°	at 14.5 mm.	(3)	1.3217 (3)
124°	at 14 mm.	(4)	cf. (4)
122.5–123.5°	at 13.5 mm.	(5)	D_4^0 = 1.3416
			1.3375 (3)

Attention is directed to the fact that C̄ is in most respects extremely similar in physical constants and chemical behavior to the isomeric glycerol α-monochlorohydrin (3-chloropropanediol-1,2) (3:9038); that C̄ is very readily partially isomerized to the latter, and that, therefore, the homogeneity of all prepns. of C̄ or reactn. prods. derived from supposedly pure C̄ must be accepted with reserve. The literature of the two glycerol monochlorohydrins is seriously entangled, and reference to the original articles must be made for supporting details.

PREPARATION OF C̄

C̄ has been isolated (3) from the mixed glycerol monochlorohydrins by fractional hydrolysis and distillation; this isolation has been confirmed (4) (6) by methods based on the slower condensation of C̄ with acetone (see below). — The mixture of glycerol monochlorohydrins obtd. from glycerol (1:6540) with conc. HCl at 120° for 5 hrs. under press. contains (4) 13% C̄.

Dubois, *Compt. rend.* **187**, 767–769, 949–951 (1928); *Bull. soc. chim.* (4) **47**, 570 (1930). (46) den Otter, *Rec. trav. chim.* **57**, 18–20 (1938). (47) Banerjee, Sen, *J. Indian Chem. Soc.* **9**, 509–518 (1932). (48) Smith, Wode, Widhe, *Z. physik. Chem.* **130**, 157–162 (1927). (49) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; *Cent.* **1937**, II 2433; *C.A.* **31**, 5813 (1937). (50) Bigot, *Ann. chim.* (6) **22**, 481–487 (1891).

(51) Curme, Young (to Carbide and Carbon Chem. Corpn.) Canadian 238,729, March 18, 1924; *Cent.* **1925**, I 1129; not in *C.A.* (52) Grün, Ger. 272,337, March 27, 1914; *Cent.* **1914**, I 1469–1470; *C.A.* **8**, 2604 (1914): Ger. 227,901, Sept. 3, 1914; *Cent.* **1914**, II 812; *C.A.* **9**, 1096 (1915). (53) Lourenco, *Ann.* **120**, 91 (1861) (54) Koelsch, *J. Am. Chem. Soc.* **52**, 1105–1106 (1930). (55) von Richter, *J. prakt. Chem.* (2) **20**, 193–195 (1879). (56) Tsunoo, *Ber.* **68**, 1342 (1935). (57) Rathsburg, Gawlich, *Chem Ztg.* **65**, 426–427 (1941); *Cent* **1942**, I 651; *C.A.* **37**, 3273 (1943). (58) Grün, Boedecker, *Ber.* **43**, 1058, Note 1 (1910). (59) Olivier, Berger, *Rec. trav. chim.* **41**, 639–640 (1921). (60) Drozdov, Chernov, *J. Gen Chem.* (*U.S.S.R.*), **4**, 1305–1309 (1934); *Cent.* **1936**, I 4549, *C.A.* **29**, 3306 (1935).

[illegible] 1933, I 2870; [*C.A.* **27**, 2455 [illegible] , 1927; *Cent.* **1928**, I 410; [illegible] –397 (1925). (64) Smith, *Z. physik. Chem.* **83**, 349–352 (1912). (65) Smith, Lindberg, *Ber.* **61**, 1709–1717 (1928). (66) Thiess, Müller (to M.L.B.), Ger. 405,384, Oct. 31, 1924; *Cent.* **1925**, I 1527; not in *C.A.* (67) Carius, *Ann.* **124**, 222–224 (1862) (68) Nef, *Ann.* **335**, 232 (1904). (69) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937, *Cent.* **1937**, II 2433; [*C.A.* **31**, 2612 (1937)]. (70) Marple, Evans (to Shell Development Co.), U.S. 2,248,635, July 8, 1941; *C.A.* **35**, 6599 (1941).

(71) Nivière, *Bull. soc. chim.* (4) **15**, 464–465 (1914). (72) Lüders, (*a*) Ger. 291,541, April 20, 1916; *Cent.* **1916**, I 913; *C.A.* **11**, 1018 (1917); (*b*) [illegible] *C.A.* **11**, 1519 (1917). (73) Lüders, Emn [illegible] **1915**, II 238. (74) Fairbourne, Stephens, [illegible] 1625 (1920). (76) Bailly, Gaumé, *Compt.* [illegible] (1924). (77) King, Pyman, *J. Chem. Soc.* **105**, 1255 (1914). (78) Bailly, *Ann. chim.* (9) **6**, 127–137 (1916). (79) Oechslin (to Étab Poulenc Frères), Brit 191,028, Feb. 14, 1923; *Cent.* **1923**, IV 721, *C.A.* **17**, 2887 (1923): French 556,366, July 19, 1923; *Cent.* **1923**, IV 721, not in *C.A.* (80) Fairbourne, Gibson, Stephens. *J. Soc Chem. Ind.* **49**, 1069 (1930).

(81) Smith, Nilsson, *J. prakt. Chem.* (2) **162**, 63–70 (1943). (82) Hill, Pyman, *J. Chem. Soc.* **1929**, 2236–2238. [illegible] 226,454, Oct. 4, 19[illegible] *Chem. Soc.* **51**, 1947 [illegible] Carter, *J. Am. Ch*[illegible] **1930**, 2542–2546. [illegible] Jones, *J. Chem. Soc.* **1933**, 167. [illegible]

21, 276–277 (1899). [illegible]

(102) Chem Fabrik Griesheim-Elektron, [illegible] 17; [*C.A.* **9**, 356 (1915)]. (103) Nieuwland, [illegible] 930). (104) Killian, Hennion, Nieuwland, [illegible] egg, Chermette (to Soc. Chim Usines du [illegible] 3370; [*C.A.* **20**, 1243 (1926)]. (106) Van Romburgh, *Rec. trav. chim* **1**, 186–187 (1882). (107) Smith, *Z. physik. Chem.* **102**, 64–65 (1922). [illegible] 11–4343 [illegible] *J. Am.* [illegible] (114) [illegible] (115) [illegible] *physiol.*

3:9040 1,4-DICHLOROBUTADI-YNE-1,3 C_4Cl_2 Beil. I — I_1— I_2-(246)
(Dichlorobiacetylene) Cl—C≡C—C≡C—Cl

M.P. 1-3° (1)

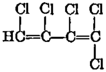
Long colorless ndls., which can be distilled under N_2 yielding a colorless oil (1). — $\bar{C}$ has odor of dichloroacetylene; readily polymerizes to an insol. dark brown explosive material. — $\bar{C}$ explodes at 73° (1).

[For prepn. of $\bar{C}$ from diacetylene [Beil. I-266] by actn. of alk. hypochlorite soln. in cold and absence of light see (1) (2) (3).]

$\bar{C}$ dislvd. in $CHCl_3$ and stood 1 day with I_2 in $CHCl_3$ adds 2 moles I_2 yielding (1) 1,4-dichloro-1,2,3,4-tetraiodobutadiene-1,3, which after careful recrystn. from C_6H_6/pet. ether has m.p. 155-157° (1).

3:9040 (1) Straus, Kollek, Hauptmann, *Ber.* **63**, 1893-1894 (1930). (2) I.G., Brit. 333,946, Sept. 18, 1930; *Cent.* **1931**, I 523. (3) I.G., Ger. 495,787, April 17, 1930.

3:9044 1,1,2,3,4-PENTACHLOROBUTADIENE-1,3 C_4HCl_5 Beil. I - 250 I_1— I_2-(225)

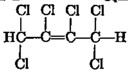


B.P. 125° at 70-80 mm. (1)

[From 2,3,4,5,5-pentachloropentadien-2,4-oic acid-1 [Beil. II-482] by boilg. with aq., then distilling with steam; the structure of the acid (and therefore of $\bar{C}$) is disputed (2). — For two other materials (b.p. 193-200° at 720 mm.) having the composition C_4HCl_5, obtd. from trichloroethylene (3:5170) with $AlCl_3$, but thought *not* to be identical with $\bar{C}$, see (3).]

3:9044 (1) Zincke, Kuster, *Ber.* **26**, 2113 (1893). (2) Zincke, *Ann.* **296**, 143 (1897). (3) Kaufler, *Ann.* **433**, 48-51 (1923).

3:9046 1,1,2,3,4,4-HEXACHLOROBUTENE-2 $C_4H_2Cl_6$ Beil. S.N. 11
(Liquid stereoisomer)



B.P. 97-98° at 10 mm. (1) D_{15}^{15} = **1.651 (1)** n_D^{-} = **1.53313 (1)**

[*See also solid stereoisomer* (3:1945).]

Colorless oily liq. with agreeable odor.

[For formn. of $\bar{C}$ (together with its solid stereoisomer (3:1945)) by actn. of Cl_2 upon the high-boilg. fraction obtd. in the prepn. of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1); for formn. of $\bar{C}$ from the liq. stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3 + Cl_2 see (1).]

3:9046 (1) Müller, Hüther, *Ber.* **64**, 589-600 (1931); *C.A.* **25**, 3956-3957 (1931).

[For formn. of $\bar{C}$ (together with the isomeric α-monochlorohydrin) from a mixt. of monochlorohydrin diacetates with abs. MeOH contg. dry HCl gas see (7).]

[The mixture of the two glycerol monochlorohydrins obtd. from allyl alcohol (1:6145) by addn. of HOCl (1) (8) (5) cf. (6) (9) (10) (11) (13) or from epichlorohydrin (3:5358) q.v. by addn. of aq. in pres. of acids has been shown (12) to be essentially similar to that obtd. from glycerol with HCl, although different proportions of α- and β- isomers might be anticipated (3).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction of $\bar{C}$. [$\bar{C}$ with Na/Hg in aq. alc. HCl gives (8) trimethylene glycol (1:6490).]

Behavior with aq. alkalies. [$\bar{C}$ with aq. alk. loses HCl and ring-closes to 3-hydroxy-1,2-epoxypropane (glycidol = epihydrin alcohol): this reactn. occurs with $\bar{C}$ very much more slowly than for the isomeric α-monochlorohydrin (3:9038); for its use in detn. of purity of $\bar{C}$ see (6) (3) (13) (14).]

Behavior with alkali cyanides. [$\bar{C}$ in 95% alc. with aq. KCN (or NaCN) in s.t. at 100° for 36 hrs., followed by hydrolysis, does *not* (6) give the expected β,β'-dihydroxyisobutyric acid but instead gives (35% yield (6)) the lactone of β,γ-dihydroxy-*n*-butyric acid (β-hydroxy-*n*-butyro-γ-lactone), m.p. 22.5–26° (6), i.e., the same prod. similarly obtd. from glycerol α-monochlorohydrin (3:9038).]

Behavior with NaI. [$\bar{C}$ with dry NaI in anhydrous acetone in s.t. at 100° for 12 hrs. gives (18% yield (15)) glycerol β-mono-iodohydrin, m.p. 52–53° (15).]

Behavior with acetone. [$\bar{C}$ in acetone with P_2O_5 at 2–7° gives (57% yield (4)) a condensation prod., "acetone-β-chlorohydrin," $C_6H_{11}O_2Cl$, b.p. 161.5–162 2° cor. at 757 mm., $D_4^{15} = 1.1344$, $n_D^{15} = 1.4487$, this condensation occurs less readily, however, than the analogous reactn. for glycerol α-monochlorohydrin (3:9038), and removal of the latter by this means has been used (4) to enrich the proportion of $\bar{C}$ in a mixt. of the two]

—— **Glycerol β-monochlorohydrin α-acetate:** oil, b.p. 230° at 760 mm., 230–234° cor. at 750 mm. (10), $D_{15}^{15} = 1\ 235$ (10). (See 3:6648.)

—— **Glycerol β-monochlorohydrin α,α'-diacetate:** oil, b.p. 101–102° at 4 mm. (15).

—— **Glycerol β-monochlorohydrin α-benzoate:** unreported.

—— **Glycerol β-monochlorohydrin α,α'-dibenzoate:** oil, b.p. 210–211° at 1.5 mm. (15).

—— **Glycerol β-monochlorohydrin α,α'-*bis*-(*p*-nitrobenzoate):** m p. 121–122° (16) (7). [Prepd. indirectly; note that this prod. depresses the m.p. of authentic glycerol α-monochlorohydrin *bis*-(p-nitrobenzoate), m.p. 108–109° u.c. (7).]

—— **Glycerol β-monochlorohydrin α-(*N*-phenylcarbamate):** m.p. 133–136° (6), 131–133° remelting at 133° (12). [From $\bar{C}$ with phenyl isocyanate in 6% yield (6); note that, for the corresp. deriv. of glycerol α-monochlorohydrin, m.p. is 128–129° (12).]

3:9039 (1) Hanriot, *Ann. chim.* (5) **17**, 73–75, 76–78 (18
949–950 (1931). (3) Smith, *Z physik. Chem.* **94**, 723–7
509–516 (1931). (5) Read, Hurst, *J. Chem. Soc.* **121**,
Spieth, Hutton, *J Am. Chem. Soc.* **53**, 3169–3171 (19
773–776 (1932). (8) Henry, *Ber* **5**, 449 (1872): *Bull acad. roy. Belg* (3) **33**, 110–114; *Cent.* **1897**, I 741. (9) Esser, Ward (to du Pont Co), U.S. 1,594,608, Aug 3, 1926; *Cent.* **1926**, II 1693; [*C.A.* **20**, 3170–3171 (1926)]. (10) Wegscheider, Zmerzlikar, *Monatsh.* **34**, 1071–1072 (1913).
07 (1943).
Chem. **92**,
ss, *J. Am.*

$\bar{C}$ is volatile with steam (use in sepn. from accompanying resin (1).)

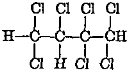
$\bar{C}$ reduces Tollens' soln. but not $NH_4OH/AgNO_3$ without alkali (1).

$\bar{C}$ is not attacked by boilg. 0.1% $KMnO_4$ (1).

$\bar{C}$ on boilg. with excess $N/10$ alc. KOH splits off 2.34–2.6 moles HCl but $\bar{C}$ cannot be titrated (1).

3:9054 (1) Prins, *Rec. trav. chim.* **56**, 123–124 (1937).

3:9056 1,1,2,2,3,4,4-HEPTACHLOROBUTANE $C_4H_3Cl_7$ Beil. S.N. 10



B.P. 137.5° at 13.5 mm. (1) D^{20}_{20} = **1.742 (1)** n^{20}_D = **1.5407 (1)**

97.5° at 2 mm. (1)

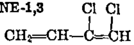
[For prepn. of $\bar{C}$ (60% yield (1) together with other products) from 1,2-dichloroethylene (3:5030) + pentachloroethane (3:5880) + $AlCl_3$ for 12 days at 40° see (1).]

$\bar{C}$ in CCl_4 gives with $AlCl_3$ a yel. color; no HCl is evolved on boilg., and on addn. of water the solution is completely decolorized (1).

$\bar{C}$ with Zn dust in alc. gives (50% yield (1)) of a trichlorobutadiene, b.p. 161°, 52° at 12 mm. (1).

3:9056 (1) Prins, Rec. trav. chim. ***56****, 124–125 (1937).*

3:9057 1,2-DICHLOROBUTADIENE-1,3 $C_4H_4Cl_2$ Beil. S.N. 12



B.P. 60–65° at 105 mm. (4) D^{15}_{15} = **1.207 (1)** n^{15}_D = **1.5078 (1) (5)**

46.75–47.5° at 85 mm. (5)

60–65° at 40 mm. (1) D^{15}_4 = **1.199 (5)** n^7_D = **1.4698 (2)**

$\bar{C}$ polymerizes slower than chloroprene (3:7080) yielding a rubberlike polymer which on vulcanization gives an ebonite-like subst. (1).

[For prepn. of $\bar{C}$ (56% yield (4)) from 1-chloro-2-vinylacetylene (3:7070) by treatment as directed at room temp. with conc. HCl + CuCl + NH_4Cl see (4); for formn. from vinylacetylene + Cl_2 see (3); for prepn. of $\bar{C}$ from 1,2,4-trichlorobutene-2 (3:9062) with EtOH/KOH see (5).]

$\bar{C}$ on oxidn. with $KMnO_4$ yields (3) oxalic acid dihydrate (1:0445). — $\bar{C}$ on ozonization in CCl_4 (3) yields oxalic acid (1:0535) and formic acid (1:1005); under specified conditions, however, *α,β*-dichloroacrylic acid (3:2265), m.p. 85–86°, has been isolated (3).

$\bar{C}$ fails to add maleic anhydride (3). — [For behavior of $\bar{C}$ with HOBr or with HgO + I_2 + MeOH see (6).]

R. **1935**, No. 2, 189–226;
(1936). (2) Klebanskiĭ,
nl. **1936**, I 3414; *C.A.* **30**,
t. 389,122, April 4, 1933;
56 (1943); *C.A.* **38**, 1467
. **38**, 329–330 (1944).

3:9048 HEXACHLOROBUTENE-X $C_4H_2Cl_6$ Beil. S.N. 11

B.P. 106–107.5° at 14 mm. (1)

[For formn. of C̄ from 1,1,2,2,3,4,4-heptachlorobutane (3:9056) with conc. aq. KOH see (1).]

C̄ reduces Tollens' reagt. (1).

3:9048 (1) Prins, *Rec. trav. chim.* **56**, 125 (1937); *Cent.* **1937**, I 3308; *C.A.* **31**, 2999 (1937).

3:9050 HEXACHLOROBUTENE-Y $C_4H_2Cl_6$ Beil. S.N. 11

B.P.	M.P.		
125.5° at 25 mm. (1)	**9.5–11° (1)**	D_4^{20} = **1.6880 (1)**	n_D^{20} = **1.5442 (1)**

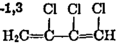
[For formn. of C̄ (together with other products) by actn. of F_2 on trichloroethylene (3:5170) see (1).]

C̄ does not add Cl_2 or Br_2 in sunlight (1).

C̄ differs (1) in prop. from the solid stereoisomer (3:1945) of 1,1,2,3,4,4-hexachlorobutene-2.

3:9050 (1) Miller, *J. Am. Chem. Soc.* **62**, 343 (1940).

3:9052 1,2,3-TRICHLOROBUTADIENE-1,3 $C_4H_3Cl_3$ Beil. S.N. 12



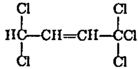
B.P. 33–34° at 7 mm. (1) (2) D_4^{20} = **1.4060 (1)** n_D^{20} = **1.5262 (1)**

[For prepn. of C̄ from 1,2,2,3,4-pentachlorobutane (3:9070) (55% yield of C̄ together with 25% yield 2,3,3,4-tetrachlorobutene-1 (3:9060)) with alc. KOH for 2 hrs. at room temp. see (1) (2).]

C̄ after addition of hydroquinone can be distd. in vac. (1). — C̄ polymerizes more slowly than 2,3-dichlorobutadiene-1,3 (3:5220); under ordinary conditions C̄ changes in 10–12 days to a jelly-like mass contg. 50% unchanged C̄, after a month polymerization to a dark-colored soft friable mass is apparently complete (1).

3:9052 (1) Carothers, Berchet, *J. Am. Chem. Soc.* **55**, 2004–2008 (1933) **(2)** Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934, *Cent.* **1935**, I 3724; *C.A.* **28**, 5716 (1934).

3:9054 1,1,1,4,4-PENTACHLOROBUTENE-2 $C_4H_3Cl_5$ Beil. S.N. 11

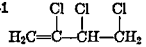


B.P. 78.5–80° at 11 mm. (1) D_{22}^{22} = **1.611 (1)** n_D^{22} = **1.5518 (1)**

76–77.0° at 10 mm. (1) D_{21}^{21} = **1.612 (1)** n_D^{21} = **1.5538 (1)**

[For prepn. of C̄ (in small yield and with much resinification (1)) from either trichloroethylene (3:5170) + 1,1,2-trichloroethane (3:5330) + $AlCl_3$ for 7 days at 40°, or from 1,2-dichloroethylene (3:5030) + 1,1,1,2-tetrachloroethane (3:5555) + $AlCl_3$ for 10 days at 40°, see (1).]

3:9064 2,3,4-TRICHLOROBUTENE-1 $C_4H_5Cl_3$ Beil. S.N. 11
(1,2,3-Trichlorobutene-3)



B.P. 40–41° at 10 mm. (1) **D_4^{20} = 1.3430 (1)** **n_D^{20} = 1.4944 (1)**
37–41° at 10 mm. (2)
36–40° at 6 mm. (2)

[For formn. of C̄ from 4-chlorobutadiene-1,2 (3:7225) (together with 1,2,4-trichlorobutene-2 (3:9062)) especially at low temps., e.g., −60 to −70°, see (1). Note that at 40–60° C̄ formed by this reactn. reacts further with the by-product 1,2,4-trichlorobutene-2 (3:9062) to yield (1) as the principal product 1,2,3,3-tetrachlorobutane (3:9080) q.v.; for formn. of C̄ from 2-chlorobutadiene-1,3 (Chloroprene) (3:7080) with Cl_2 see (2) (3).]

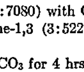
C̄ with alk. as specified (2) gives 2,3-dichlorobutadiene-1,3 (3:5220), b.p. 98° at 760 mm. (2).

C̄ on htg. with 2 pts. aq. + calcd. amt. powdered $CaCO_3$ for 4 hrs. at 70° *fails* (4) to hydrolyze [diff. from 1,2-dichlorobutene-2 (3:5615) or 1,3-dichlorobutene-2 (3:5550)]. — C̄ does react, however, with hot aq. K_2CO_3 losing HCl and yielding (4) alm. 100% 2,3-dichlorobutadiene-1,3 polymer (4).

C̄ on oxidn. with aq. $KMnO_4$ yields (1) α,β-dichloropropionic acid, (3:0855), m.p. 49–50°, Neut. Eq. 141 (calcd. 143) (1).

3:9064 (1) Carothers, Berchet, *J. Am. Chem. Soc.* **55**, 1628–1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3
(to du Pont), U.S. 1,964,720, July
chenko, *J. Gen. Chem.* (*U.S.S.R.*)

3:9066 1,3-DICHLORO-2-(CHLOROMETHYL)PROPENE-1 $C_4H_5Cl_3$ Beil. I —
I_1—
I_2-(181)



B.P. 62–64° at 9 mm. (1) (2)

[For formn. of C̄ (together with other products) from 1,3-dichloro-2-chloromethyl-2-nitropropane [Beil. I_2-(92)] with Na/Hg (2) or from 2-nitro-2-hydroxymethylpropanediol-1,3 [Beil. I_2-(596)] with PCl_5 (1) see (1) (2).]

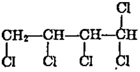
C̄ on cat. hydrogenation with Pt black in alc. yields (2) 1,3-dichloro-2-methylpropane (3:7960), b.p. 45° at 10 mm.

C̄ in $CHCl_3$ on shaking with Cl_2/aq. adds Cl_2 yielding (2) 1,1,2,3-tetrachloro-2-chloromethylpropane (3:9072), b.p. 99–101° at 12 mm. — C̄ with Br_2 in $CHCl_3$ adds Br_2 yielding (2) 1,2-dibromo-1,3-dichloro-2-(chloromethyl)propane, colorless odorless oil, b.p. 140° at 10 mm.

[For reactn. of C̄ with sodio-malonic ester see (3).]

3:9066 (1) Kleinfeller, Ber. 62, 1585–1587 (1929). (2) Kleinfeller, Ber. 62, 1594–1595 (1929). (3) Kleinfeller, Frercks, *J. prakt. Chem.* (2) **138**, 195–196 (1933).

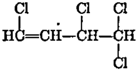
3:9068 1,1,2,3,4-PENTACHLOROBUTANE $C_4H_5Cl_5$ Beil. S.N. 10
(Liquid diastereoisomer)
(1,2,3,4,4-Pentachlorobutane
(liquid diastereoisomer))



B.P. 95.3–95.5° at 11 mm. (1)

[See also solid diastereoisomer (3:0750).]

3:9058 1,3,4,4-TETRACHLOROBUTENE-1 $C_4H_4Cl_4$ Beil. S.N. 11
(1,1,2,4-Tetrachlorobutene-3)

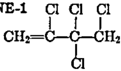


B.P. 82–83° at 17 mm. (1)

[For prepn. of C̄ from 1,2-dichloroethylene (3:5030) by polymerization in pres. of peroxide cat. see (1).]

3:9058 (1) Bauer, U.S. 2,267,712, Dec. 30, 1941; *C.A.* 36, 2564 (1942).

3:9060 2,3,3,4-TETRACHLOROBUTENE-1 $C_4H_4Cl_4$ Beil. S.N. 11
(1,2,2,3-Tetrachlorobutene-3)



B.P. 41–42° at 7 mm. (1) D_4^{20} = **1.4602** (1) n_D^{20} = **1.5133** (1)

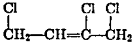
[For formn. of C̄ (25% yield (1)) from 1,2,3,3,4-pentachlorobutane (3:9070) with MeOH/KOH at room temp. for 2 hrs. (together with 55% yield 1,2,3-trichlorobutadiene-1,3 (3:9052)) see (1).]

C̄ on oxidn. with excess aq. $KMnO_4$ yields (1) α,α,β-trichloropropionic acid (3:1275), m.p. 48–50°, Neut. Eq 176 4 (calcd 177.5) (1).

[A liquid, b p. 90–110° at 25 mm., D_4^{21} = 1.473, n_D^{21} = 1.514, and believed to be a mixt. of tetrachlorobutenes, has been obtd. (2) from monovinylacetylene + Cl_2; it may or may not have contained C̄.]

3:9060 (1) Berchet, Carothers, *J. Am. Chem. Soc.* 55, 2004–2008 (1933). (2) Rengert, Schumacher, *Ber* 73, 1025–1042 (1940); *C.A.* 35, 1027 (1941).

3:9062 1,2,4-TRICHLOROBUTENE-2 $C_4H_5Cl_3$ Beil. S.N. 11
(1,3,4-Trichlorobutene-2)



B.P. 67–69° at 10 mm. (3) D_4^{20} = **1.3843** (1) n_D^{20} = **1.5175** (1)
64–65° at 10 mm. (1)
62–65° at 11 mm. (2) D_4^{15} = **1.3575** (3) n_D^{15} = **1.5121** (3)

[For formn. of C̄ from 4-chlorobutadiene-1,2 (3:7225) + Cl_2 (together with 2,3,4-trichlorobutene-1 (3:9064) and 1,2,2,3,4-pentachlorobutane) see (1) (2); for formn. of C̄ from 2-chlorobutadiene-1,3 (Chloroprene) (3:7080) + Cl_2 (together with 2,3,4-trichlorobutene-1 (3:9064) and 1,2,2,3,4-pentachlorobutane (3:9070)) see (1) (2) (3).]

C̄ with EtOH/KOH as directed (3) loses HCl giving 1,2-dichlorobutadiene-1,3 (3:9057).

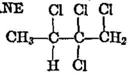
C̄ on oxidn. with aq. $KMnO_4$ yields (1) (3) chloroacetic acid (3:1370), m.p. 63°, Neut. Eq. 95.1 (calcd. 94.5) (1).

3:9062 (1) Carothers, Berchet, *J. Am. Chem. Soc.* 55, 1628–1631 (1933). (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* 1935, I 3724; *C.A.* 28, 5716 (1934). (3) Petrov, *J. Gen. Chem.* (*U.S.S R.*) 13, 102–107 (1943); *C.A.* 38, 329 (1944).

[For prepn. of $\bar{C}$ in 55% yield (1) from 2-chlorobutene-2 (3:7105) by treatment with 1 mole Cl_2 + 1.5 moles $NaHCO_3$ at 0° (accompanied by 45% yield 2,2,3-trichlorobutane (3:5680)) see (1); with Cl_2 in pres. of light and O_2 as directed see (2).]

3:9074 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939). (2) Hearne (to Shell Development Co.), U.S 2,296,614, Sept. 22, 1942; *C.A.* **37**, 1129 (1943).

3:9078 1,2,2,3-TETRACHLOROBUTANE



$C_4H_6Cl_4$ **Beil. I-119**
I_1—
I_2—

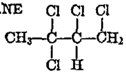
B.P. 63.0–63.5° at 11 mm. (1) D_4^{18} = **1.4276 (1)** n_C^{18} = **1.4893 (1)**

[For prepn. (100% yield (1)) from 1,2-dichlorobutene-2 (3:5615) with 1 mole Cl_2 + 1.5 moles $NaHCO_3$ at 0° see (1).]

[The product obtained (2) cf. (3) from 2,2,3-trichlorobutanol-1 (3:1336) with PCl_5 may have been impure $\bar{C}$.]

3:9078 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S R.*) **8**, 1232–1246 (1938); *C.A.* **33**, 4190 (1939). (2) Garzarolli-Thurnlaekh, *Ann.* **213**, 372–373 (1882). (3) Norton, Noyes, *Am. Chem. J.* **10**, 432 (1888).

3:9080 1,2,3,3-TETRACHLOROBUTANE



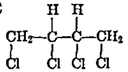
$C_4H_6Cl_4$ **Beil. S.N. 10**

B.P. 90° at 32 mm. (1) D_4^{20} = **1.4204 (1)** n_D^{20} = **1.4958 (1)**
55–57° at 10 mm. (1)

[For formn. of $\bar{C}$ (together with other products) from 1,3-dichlorobutene-2 (3:5550) at 40–60° with Cl_2 see (1). Note, however, that at very low temps. (−60 to −70°) much HCl is evolved during chlorination and the principal products are then 2,3,4-trichlorobutene-1 (3:9064), b.p. 40–41° at 10 mm. (1), and 1,2,3,3,4-pentachlorobutane (3:9070), b.p. 85° at 10 mm. (1).] [For patents on this process see (2) (3).]

3:9080 (1) Carothers, Berchet, *J Am. Chem. Soc* **55**, 1629–1631 (1933). (2) Coffman (to du Pont), U.S. 1,964,720, July 3, 1934; *Cent.* **1934**, II 3180; *C.A.* **28**, 5080 (1934). (3) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* **1935**, I 3724; *C.A.* **28**, 5716 (1934).

—— 1,2,3,4-TETRACHLOROBUTANE
(Solid isomer)



$C_4H_6Cl_4$ **Beil. I - 119**
I_1-(38)
I_2—

B.P. 130–134° at 40 mm. **M.P. 73°**

See 3:1760. *Division A: Solids.*

[For prepn. of C̄ (30–50% yield of mixed solid and liquid stereomers (1)) from 1,2-dichloroethylene (3:5030) + 1,1,2-trichloroethane (3:5330) + 1% $AlCl_3$ for 5 days at 35–40° see (1).]

C̄ in CCl_4 treated with $AlCl_3$ gives a dark violet soln. which on boilg. evolves HCl (1).

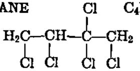
C̄ in alc. treated wih Zn dust gives (60% yield (1)) 1-chlorobutadiene-1,3 (3:7210), b.p. 68° (1).

C̄ dissolved in hot alc. and titrated with $N/10$ KOH splits off 1.51–1.59 moles HCl (1).

[A pentachlorobutane obtained (2) from trichloroethylene (3:5170) + 1,1-dichloroethane (3:5035) + $AlCl_3$ may or may not be identical with C̄.]

3:9068 (1) Prins, *Rec. trav. chim.* **56**, 121–123 (1937). (2) Consortium fur Elektrochem. Ind., Brit. 453,414, Oct. 8, 1936, *Cent.* **1937**, I 1012.

3:9070 1,2,2,3,4-PENTACHLOROBUTANE $C_4H_5Cl_5$ **Beil. S.N. 10**
(1,2,3,3,4-Pentachlorobutane)



B.P. 85° at 10 mm. (1)
78–84° at 9 mm. (2)
82–86° at 6 mm. (2)

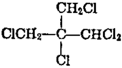
D_4^{20} = **1.5543** (1) n_D^{20} = **1.5157** (1)

[For prepn. of C̄ from 1,3-dichlorobutene-2 (3:5550) by actn. of Cl_2 at low temps. (−60 to −70°), much HCl being evolved and 2,3,4-trichlorobutene-1 (3:9064) also being formed, see (1); note also that chlorination of 4-chlorobutadiene-1,2 (3·7225) gives mixts. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which react further to yield C̄ (1).] [For patents on these processes see (2) (3).]

C̄ with alk. yields (2) both 1,2,3-trichlorobutadiene-1,3 (3.9052), b.p. 34° at 7 mm. (2), and 2,3,3,4-tetrachlorobutene-1 (3:9060), b.p. 42° at 7 mm. (2).

3:9070 *(1)* Carothers, Berchet, *J. Am Chem. Soc. 55, 1628–1631 (1933).* (2) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* **1935**, I 3724; *C A* **28**, 5716 (1934). (3) Coffmann (to du Pont), U.S. 1,964,720, July 3, 1934; *Cent* **1934**, II 3180; *C.A* **28**, 5080 (1934).

3:9072 1,1,2,3-TETRACHLORO-2-(CHLOROMETHYL)PROPANE $C_4H_5Cl_5$ **Beil. I —**
I_1—
I_2-(89)

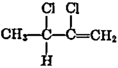


B.P. 99–101° at 12 mm. (1)

[For prepn. of C̄ from 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066) by shaking in $CHCl_3$ with Cl_2/aq. see (1).]

3:9072 (1) Kleinfeller, *Ber.* **62**, 1595 (1929).

3:9074 2,3-DICHLOROBUTENE-1 $C_4H_6Cl_2$ **Beil. S.N. 11**



B.P. 111–113° at 2 mm. (1)

3:0855 *d,l*-α,β-DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ Beil. II - 252, II_1-(111), II_2—

$$\underset{\displaystyle Cl}{\underset{|}{CH_2}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-COOH$$

M.P. 50°	(1) (10)	B.P. 210° sl. dec.	at 762 mm.	(1)
49.5°	(2)	130–133°	at 26 mm.	(3)
49–50°	(3)	112–115°	at 12 mm.	(5)
49°	(4)			
47–50°	(5)			

[For prepn. from methyl α,β-dichloropropionate (3:9103) by boilg. with 20% HCl (65% yield) see (3); from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) by oxidn. with HNO_3 see (1) (6) (7) (2) (5); from α,β-dichloroacrolein by oxidn. with HNO_3 see (7); from α-chloropropionic acid (3:6125) with Cl_2 at 45° see (8); for formn. of $\bar{C}$ from α-chloroacrylic acid (3:1445) (6) (9) or from α-chloro-β-hydroxypropionic acid (α-chlorohydracrylic acid) [Beil. III-298] (10), or α,β-dihydroxypropionic acid (glyceric acid) (11) by htg. with fumg. HCl in s.t. at 100°, see indic. refs.]

$\bar{C}$ with aq. or alc. readily loses HCl yielding (12) (6) (9) α-chloroacrylic acid (3:1445), m.p. 65°.

$\bar{C}$ in MeOH treated as directed (13) with activated Zn gives (72% yield) acrylic acid (1:1020), b.p. 140°.

[$\bar{C}$ with $SOCl_2$ gives (15) α,β-dichloropropionyl chloride (3:9032).]

$\bar{C}$ htd. with Ag_2CO_3 yields (5) α-chloro-β-hydroxypropionic acid (α-chlorohydracrylic acid).

—— **Methyl α,β-dichloropropionate:** b.p. 72–75° at 21 mm. (see 3:9103).

—— **Ethyl α,β-dichloropropionate:** b.p. 183–184° (see 3:6090). [For the *sec*-butyl, β-chloroethyl, and cyclohexyl esters of $\bar{C}$ see (3); for glycol and other esters see (14).]

—— **α,β-Dichloropropionamide:** unreported.

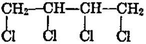
—— **α,β-Dichloropropionanilide:** unreported.

—— **α,β-Dichloropropion-*p*-toluidide:** unreported.

3:0855 (1) Henry, *Ber.* **7**, 414 (1874). (2) Bockemuller, Hoffmann, *Ann.* **519**, 190 (1935). (3) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940). (4) Simpson, *J. Am. Chem. Soc.* **40**, 676, 679 (1918). (5) Koelsch, *J. Am. Chem. Soc.* **52**, 3365 (1930). (6) Werigo, Melikov, *Ber.* **10**, 1499–1500 (1877). (7) Yarnall, Wallis, *J. Org. Chem.* **4**, 287 (1939). (8) Röhm & Haas Co., Ger. 579,654, June 29, 1931; *Cent.* **1933**, II 1587. (9) Otto, Beckurts, *Ber.* **18**, 244 (1885). (10) Melikov, *Ber.* **13**, 274 (1880).

(11) Werigo, Melikov, *Ber.* **12**, 178 (1879). (12) Werigo, Werner, *Ann.* **170**, 168 (1873). (13) Röhm & Haas Co., Ger. 575,423, Apr. 27, 1933; *Cent.* **1933**, II 133. (14) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,257,021, Sept. 23, 1941; *C.A.* **36**, 95–96 (1942). (15) Leimu, *Ber.* **70**, 1046, 1050 (1937).

3:9082 1,2,3,4-TETRACHLOROBUTANE (liquid isomer) $C_4H_6Cl_4$ Beil. I - 119
(Butadiene tetrachloride (liquid isomer); I_1-(38)
erythrene tetrachloride (liquid isomer)) I_2—

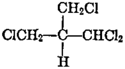


B.P. 110–111° at 40 mm. (1) (2)

For formn. and reactns. see solid form, m.p. 73° (3:1760).

3:9082 (1) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4053–4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; *Cent.* **1936**, II 3359; *C.A.* **30**, 3912 (1936).

3:9084 1,1,3-TRICHLORO-2-(CHLOROMETHYL)PROPANE $C_4H_6Cl_4$ Beil. I —
I_1—
I_2-(89)

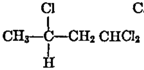


B.P. 77–80° at 9 mm. (1)

Oil with odor like CCl_4 but with irritating actn. on eyes. — Volatile with steam.
[For formn. of $\bar{C}$ in small amt. (together with other products) from 2-nitro-2-hydroxymethylpropanediol-1,3 (nitro-isobutylglycerol) with PCl_5 see (1).]

3:9084 (1) Kleinfeller, *Ber.* **62**, 1585 (1929).

3:9086 1,1,3-TRICHLOROBUTANE $C_4H_7Cl_3$ Beil. S.N. 10

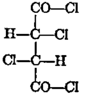


B.P. 150° at 720 mm. (1)

A trichlorobutane which may have this structure has been reported (1) when vinyl chloride (3:7004) + $AlCl_3$ at 20° reacts with the material obtd from ethylidene dichloride (3:5035) + $AlCl_3$ + chlorinated ethylenes.

3:9086 (1) Consortium für Elektrochem. Ind., Brit. 453,414, Sept. 10, 1936; *Cent.* **1937**, I 1012; *C.A.* **31**, 1046 (1937).

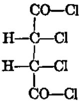
— ***d,l*-α,α′-DICHLOROSUCCINYL (DI)CHLORIDE** $C_4H_2O_2Cl_4$ Beil. II —
II_1—
II_2-(558)



B.P. 78.5° at 7 mm. **M.P. 39°**

See 3:0395. *Division A: Solids.*

3:9087 *meso*-α,α'-DICHLOROSUCCINYL(DI)CHLORIDE $C_4H_2O_2Cl_4$ Beil. II - 619
II$_1$-(267)
II$_2$-(558)



B.P. 105–106° at 45 mm. (1)
85–86° at 22 mm. (1)
79–80° at 15 mm. (2)

Colorless viscous lachrymatory oil.

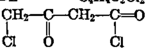
[For prepn. of $\bar{C}$ from fumaryl (di)chloride (3:5875) in CCl_4 soln. with Cl_2 in direct sunlight (100% yield (3)) (1) (2) see indic. refs.]

$\bar{C}$ with aq. reacts only very slowly on mere standing (1), but on continuous shaking with cooling readily hydrolyzes yielding (1) (2) *meso*-α,α'-dichlorosuccinic acid (3:4930).

[$\bar{C}$ with C_6H_6 + $AlCl_3$ gives (60% yield (3)) *meso*-1,2-dichloro-1,2-dibenzoylethane (*meso*-2,3-dichloro-1,4-diphenylbutandione-1,4), m.p. 167° (4) (5), accompanied under certain conditions (3) by some α,β-dichloro-γ,γ-diphenylbutyrolacetone, m.p. 141–142° (3), presumably arising from reactn. of $\bar{C}$ in the unsymmetrical (phthalide type) form.]

3:9087 (1) Michael, Tissot, *J. prakt. Chem.* (2) **46**, 394–395 (1892). (2) Holmberg, *J. prakt. Chem.* (2) **84**, 148 (1911). (3) Lutz, *J. Am. Chem. Soc.* **49**, 1109–1110 (1927). (4) Conant, Lutz, *J. Am. Chem Soc.* **47**, 885–886 (1925). (5) Lutz, *J. Am. Chem. Soc.* **48**, 2908, 2911 (1926).

3:9088 γ-CHLOROACETOACETYL CHLORIDE $C_4H_4O_2Cl_2$ Beil. III —
(γ-Chloro-β-keto-*n*-butyryl chloride) III$_1$—
III$_2$—



B.P. 117–119° at 17 mm. (1) D_4^{20} = **1.4397 (1)** n_D^{20} = **1.4860 (1)**
93–96° at 8 mm. (1)

Orange-colored liq. which fumes in air.

[For prepn. of $\bar{C}$ from acetylketene (ketene dimer) (2) (3) with Cl_2 in cold CCl_4 soln. see (1).]

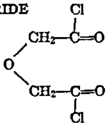
$\bar{C}$ with aq. yields chloroacetone (3:5425) + CO_2 + HCl (note that this method gives chloroacetone free from higher chlorination products (3)).

[$\bar{C}$ with excess abs. EtOH at 0° gives (1) (3) ethyl γ-chloroacetoacetate (3:6375).]

$\bar{C}$ with aniline in C_6H_6 yields (1) (3) γ-chloroacetoacetanilide, cryst. from ether, m.p. 140–141° (1).

3:9088 (1) Hurd, Abernathy, *J. Am. Chem. Soc.* **62**, 1147–1148 (1940). (2) Hurd, Williams, *J. Am. Chem. Soc.* **58**, 962–968 (1936). (3) Boese, *Ind. Eng. Chem.* **32**, 16–22 (1940).

3:9092 DIGLYCOLOYL DICHLORIDE $C_4H_4O_3Cl_2$ Beil. S.N. 220



B.P. 116° at 12 mm. (1)

Colorless oily liq. with odor suggesting succinyl dichloride (3:6200).

[For prepn. of C̄ from diglycolic acid (1:0495) by susp. in $CHCl_3$ and treatment with PCl_5 see (1) (note also that insufficient PCl_5 leads (1) to diglycolic anhydride, m.p. 97°, b.p. 120° at 12 mm. (3)); for mfg. from α,α'-dichlorodimethyl ether (3:5245) by treatment at 25–50° and elevated press. with CO and suitable catalysts such as $AlCl_3$ or $ZnCl_2$ see (2).]

C̄ with excess MeOH yields (1) (3) dimethyl diglycolate, m.p. 35° (3), 36° (1).

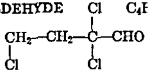
C̄ with aq. readily hydrolyzes (1) yielding diglycolic acid (1:0495); for the anilide, *p*-toluidide, and other derivs. corresp. to C̄ see the acid (1:0495).

3:9092 (1) Anschutz, Biernaux, *Ann.* **273**, 64–65 (1893). (2) Scott (to du Pont Co.), U.S. 2,084,284, June 15, 1937, *Cent* **1937**, II 2261; *C.A.* **31**, 5383 (1937). (3) Darapsky, Stauber, *J. prakt. Chem.* (2) **146**, 212 (1936).

3:9094 α,α,γ-TRICHLORO-*n*-BUTYRALDEHYDE $C_4H_5OCl_3$ Beil. I-665

I_1—

I_2—



No physical consts. on C̄ are reported; it is characterized only as a liquid which at −78° becomes a glassy solid (1). — Spar. sol. aq. (1).

[For prepn. of C̄ from α,γ-dichlorocrotonaldehyde [Beil. I-731], with dry HCl gas at 0° see (1).]

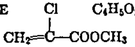
C̄ oxidizes only very slowly in air but with fumg. HNO_3 in cold gives (1) α,α,γ-trichloro-*n*-butyric acid (3:1831), m.p. 73–75° (1).

C̄ does *not* add aq. to form a hydrate but on shaking with satd. aq. $NaHSO_3$ soln. evolves heat and ppts. a $NaHSO_3$ cpd (1).

C̄ on boilg. with aq. contg. $BaCO_3$ gives an amorphous prod., very easily sol. in aq. and possessing carbohydrate characteristics; for details see (2).

3:9094 (1) Natterer, *Monatsh.* **4**, 551 (1883). (2) Natterer, *Monatsh.* **5**, 251–255 (1884).

3:9096 METHYL α-CHLOROACRYLATE $C_4H_5O_2Cl$ Beil. S.N. 163



B.P. 57–59° at 55 mm. (1) **D_4^{20} = 1.189 (1)** **n_D^{20} = 1.4420 (11)**
41–44° at 28 mm. (11) **1.4400 (1)**

[For prepn. of C̄ from methyl α,β-dichloropropionate (3:9103) by distn. with quinoline (yield: 73% (1), 60% (11)) or other dehydrochlorinating agent such as Na_2CO_3 (2) see indic. refs.; from trichloroethylene (3:5170) with CH_2O + MeOH + H_2SO_4 + $CuCO_3$ as directed (73% yield) see (10).]

[C̄ readily polymerizes on standing, especially in light or pres. of peroxides (for study of polymers and polymerization see (1)). For examples of industrial prepn. and use of polymers of C̄ for molding resins, etc., see (3) (4) (5) (6); for examples of co-polymers of C̄ with butadiene-1,3 or chloroprene (7), styrene (8), or vinyl acetate (9) see indic. refs.]

[For comments on other esters of C̄ see α-chloroacrylic acid (3:1445).]

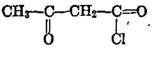
[For study of ester interchange of C̄ with various alcohols see (11).]

3:9096 (1) Marvel, Cowan, *J. Am. Chem. Soc.* **61**, 3156–3160 (1939). (2) Pollack (to Pittsburgh Plate Glass Co.), U.S. 2,245,547, June 10, 1941; *C.A.* **35**, 5908 (1941); Brit. 536,806, May 28, 1941; *C.A.* **36**, 1614 (1942). (3) Röhm & Haas Co., Brit. 411,860, June 13, 1934; *Cent.* **1935**,

I 1628–1629; *C.A.* 28, 6956 (1934). (4) Ireland, Brit. 527,494, Oct. 10, 1940; *C.A.* 35, 7065 (1941). (5) Strain, Pollack (to Pittsburgh Plate Glass Co.), U.S. ...
35,
C.A
No
194
264
194
No
194
C.A. 38, 1751 (1944).
(11) Frank, David, Drake, McPherson, *J. Am. Chem. Soc.* 66, 1509–1510 (1944).

3:9098 ACETOACETYL CHLORIDE $C_4H_5O_2Cl$ Beil. III —

(β-Keto-*n*-butyryl chloride) IIIₗ— III₂—



This compound cannot be preserved at temperatures above −20° (1) cf. (4); m.p. −50 to −51° (1).

[For prepn. of C̄ from acetylketene (ketene dimer) (2) (3) (5) with dry HCl gas at −7 to −50° see (1).] [For anal. of C̄ by reactn. with dil. alk. see (1).]

C̄ on warming to room temp. undergoes bimolecular condensation with elimination of 2 HCl and yields (1) dehydroacetic acid (1:0700), m.p. 109°.

C̄ in dry ether at −60° treated with abs. EtOH gives (27% yield (1)) ethyl acetoacetate (1:1710).

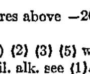
C̄ in dry ether at −60° treated with aniline gives (49% yield (1)) acetoacetanilide [Beil. XII 518, XII₁-(275)], m.p. 85°; note, however, that C̄ with aniline at room temp. yields ... acid-3 (1-phenyllutidonecarboxylic acid-3) ... Eq. calcd. 243, found 235 (1).

C̄ with C_6H_6 + $AlCl_3$ or with C_6H_5MgBr in ether at −50° gives (27% and 12% yield respectively (1)) benzoylacetone (1:1450), m.p. 59° (1).

3:9098 (1) Hurd, Kelso, *J. Am. Chem. Soc.* 62, 1548–1549 (1940). (2) Hurd, Abernathy, *J. Am. Chem. Soc.* 62, 1147–1148 (1940). (3) Hurd, Williams, *J. Am. Chem. Soc.* 58, 962–968 (1936). (4) Staudinger, Schotz, *Ber.* 53, 1109 Note 1 (1920). (5) Boese, *Ind. Eng. Chem.* 32, 16–22 (1940).

3:9098-A METHYL (CHLOROFORMYL)ACETATE $C_4H_5O_3Cl$ Beil. II - 582

(Carbomethoxyacetyl chloride) II₁-(252) II₂—



B.P. 57–59° at 12 mm. (1)

[*See also ethyl (chloroformyl)acetate* (3:9246).]

Note that C̄ is both an acid chloride and an ester; it comprises the half acid chloride/half methyl ester of malonic acid (1:0480).

[For prepn. of C̄ from potassium salt of methyl hydrogen malonate with $SOCl_2$ in dry ether (68% yield) see (1).]

C̄ on htg. or on repeated distn. or by action of quinoline in dry ether at 0° loses HCl and undergoes condensation to methyl 6-methoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. XVIII₁-(540)], ndls. from $CHCl_3$, m.p. 148–150° (1) cf. (2).

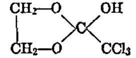
· Ⓓ ω-(Carbomethoxyacet)anilide: ndls. from ether/pet. eth., m.p. 42–43° (1). [From C̄ with aniline (1).]

—— ω-(Carbomethoxyacet)-*p*-toluidide: unreported.

3:9098-A (1) Staudinger, Becker, *Ber.* **50**, 1019–1020 (1917). (2) Leuchs, *Ber.* **39**, 2643 (1906).

3:9099 β-HYDROXYETHYL TRICHLOROACETATE (A) $HOCH_2CH_2—O—CO.CCl_3$ $C_4H_5O_3Cl_3$ Beil. S.N. 160, 2691

(2-Hydroxy-2-(trichloromethyl)-1,3-dioxolane)

 (B)

B.P. 130–140° at 12 mm. (1)			n_D^{25} = 1.4762 (3)
89° at 1.75 mm. (2)			
83° at 0.8 mm. (2)		D_4^{20} = 1.532	n_D^{20} = 1.48378 (2)
68° at 0.025 mm. (3)			1.4775 (3)

Note that C̄ may react either in the ester form (A) or the dioxolane form (B) and doubtless exists as a tautomeric equilibrium of both; in this equilibrium, however, form (A) probably predominates (2), but variations in the equilibrium may account for the observed variation in n_D^{20} (see above).

Colorless odorless oil, spar. sol. aq. (2). — C̄ on long stdg. is claimed (2) to disproportionate to ethylene glycol *bis*-(trichloroacetate) (not, however, otherwise described in the literature) and ethylene glycol (1 6465). — C̄ on attempted distn at usual water-pump vac. (14–17 mm.) (3) or C̄ in presence of a trace of pyridine (3) decomposes yielding monomeric ethylene glycol carbonate [Beil. XIX-100], m.p 38°, and $CHCl_3$ (3:5050).

[For prepn. of C̄ from ethylene glycol (1:6465) with trichloroacetyl chloride (3:5420) in 1,4-dioxane soln. (82% yield (2)) or from ethylene oxide (1:6105) with trichloroacetic acid (3:1150) (28% yield based on latter (1) (3)) see indic. refs.]

C̄ on shaking with aq. and simultaneously titrating with $N/10$ aq. NaOH hydrolyzes to ethylene glycol (1:6465) and trichloroacetic acid (3:1150) as shown by Sap Eq. of 207.8 (2) (calcd. 207.5).

[C̄ with diazomethane (1) best in CCl_4 soln. (2) gives (yields: 78% (2), 39% (1)) the methyl ether corresp. to structure (B), viz., 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, pr. tbls. from alc., m.p. 78–78.5° (1), 77–78° (2) (4), b.p. 114–115° at 12 mm. (4), 112–113° at 10 mm. (1); this product although resistant to saponification by alkalies is hydrolyzed by dil. acids (4). — Note that the isomeric methyl ether corresponding to structure (A), viz., β-methoxyethyl trichloroacetate, although not obtainable from C̄, has nevertheless been prepd. (82% yield (4)) from β-methoxyethanol (methyl "cellosolve") (1:6405 with trichloroacetyl chloride (3:5420), has quite different physical props., viz., m.p. 14 6–14 8° (4), b.p. 92–93° at 10 mm. (4), and is easily hydrolyzed (4) on shaking with aq. alone to β-methoxyethanol (1:6405) and trichloroacetic acid (3:1150). — Note also that the first of the above two methyl ethers, i e , 2-methoxy-2-(trichloromethyl)-1,3-dioxolane, by *trans*-esterification with alcohols (e g., EtOH (2), *n*-PrOH (4), *n*-BuOH (2)) can be converted to its higher homologs.]

C̄ with acid chlorides gives esters corresp. to the acylic structure (A): e.g., C̄ with AcCl (3:7065) gives (71% yield (4)) the mixed ester, ethylene glycol acetate-trichloroacetate (β-acetoxyethyl trichloroacetate) b.p. 122° at 11 mm. (4); C̄ with $SOCl_2$ gives (70% yield (4)) β-chloroethyl trichloroacetate (3:6510).

3:9099 (1) Meerwein, Hinz, *Ann* **484**, 16–17 (1930). (2) Meerwin, Sönke, *J. prakt. Chem.* (2) **137**, 295–298, 308–311 (1933). (3) Hibbert, Grieg, *Can. J. Research* **4**, 261–263 (1931). (4) Meerwin, Sönke, *Ber.* **64**, 2375–2381 (1931).

3:9100 *d,l*-β-CHLORO-*n*-BUTYRYL CHLORIDE $C_4H_6OCl_2$ Beil. II - 278

$$\begin{array}{l} CH_3.CH.CH_2.C{=}O \\ \quad\;\; | \qquad\quad\;\; | \\ \quad\; Cl \qquad\;\; Cl \end{array}$$

Beil. II - 278; II_1—; II_2-(253)

B.P. 67–69° at 41 mm. (1)
65–67° at 40 mm. (2) (3)
51–53° at 21 mm. (4) (6)
40–41° at 12 mm. (2)

$D_4^{20.25} = 1.2163$ (4)

$n_D^{20} = 1.4525$ (3)
1.4511 (4)

[For prepn. of C̄ from β-chloro-*n*-butyric acid (3:0035) with $SOCl_2$ (4) (6) (3) (90% yield (2)) see indic. refs.; from *n*-butyryl chloride (3:7370) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (55% yield C̄ + 15% α- (3:5570) and 30% γ- (3:5970) isomers (3)) or with Cl_2 in CCl_4 (1) see indic. refs.]

[C̄ with methyl *p*-tolyl ether (1:7495) + $AlCl_3$ in CS_2 yields (4) 3-(β-chloro-*n*-butyryl)-4-methylphenol (b.p. 167–170° at 20 mm. (4)) which in alc. soln. on addn. of dil. Na_2CO_3 loses HCl yielding 2,6-dimethylchromanone, m.p. 54–55° (5).]

C̄ with benzene + $AlCl_3$ in CS_2 yields (6) (by Friedel-Crafts reactn. of both halogen atoms) β-phenylbutyrophenone (phenyl β-phenyl-*n*-propyl ketone) [Beil. VII-453], m.p. 74° (6).

C̄ on hydrolysis with aq. yields β-chloro-*n*-butyric acid (3:0035) q.v. (note, however, that hydrolysis with alk. will cause loss of HCl and formn. of crotonic acid (1:0425).

For the anilide, *p*-toluidide, and other derivs. corresp. to C̄ see β-chloro-*n*-butyric acid (3:0035).

3:9100 (1) Michael, *Ber.* **34**, 4052 (1901). (2) Abderhalden, Fleischmann, *Fermentforschung*, **10**, 203 (1928); *Cent.* **1929**, I 2318; *C.A.* **23**, 1388 (1929). (3) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 928 (1940). (4) von Auwers, *Ann.* **421**, 37–39 (1921). (5) von Auwers, *Ber.* **52**, 128 (1919). (6) von Auwers, Müller, *J. prakt. Chem.* (2) **137**, 128 (1933).

3:9101 β-CHLORO-ISOBUTYRYL CHLORIDE $C_4H_6OCl_2$ Beil. II - 295

$$\begin{array}{l} CH_2{-}CH{-}C{=}O \\ \;| \qquad\; | \qquad | \\ Cl \quad\; CH_3 \;\; Cl \end{array}$$

Beil. II - 295; II_1—; II_2—

B.P. 171–172° at 765 mm. (1)
151–152° (2)

$n_D^{20} = 1.4542$ (2)

Because of the serious disagreement in b.p. and the lack of data to decide between them, C̄ is placed in this division.

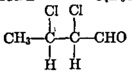
[For prepn. of C̄ from isobutyryl chloride (3:7270) with Cl_2 in CCl_4 soln. (30–40% yield C̄ + 60–70% α-isomer (3:5385) (1)), with Cl_2 in activating light (3) (6), or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (80% yield C̄ + 20% α-isomer (3:5385) (2)), see indic. refs.; for formn. of C̄ from phosgene (3:5000) + propylene + cat. see (5).]

C̄ as liq. with dehydrohalogenating cat. loses HCl giving (4) α-methacryloyl chloride.

C̄ with aniline gives (1) (2) β-chloro-isobutyranilide, m.p. 109.0–109.5° (2), 104–105° (1); note that the isomeric α-dichloro-isobutyranilide has m.p. 71–71.5° (2), 69–70° (1).

3:9101 (1) Michael, Garner, *Ber.* **34**, 4054–4055 (1901). (2) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (3) Schmidt, Schloffer (to I.G.), Ger. 738,398, July 15, 1943; *C.A.* **38**, 3992 (1944). (4) I.G., French 873, 389, July 7, 1942; *Cent.* **1942**, II 2535; not in *C.A.* (5) Reid (to du Pont Co.), U.S. 2,028,012, Jan. 14, 1936; *Cent.* **1936**, II 866; *C.A.* **30**, 1387 (1936). (6) Schmidt, Schloffer (to I.G.), Ger. 738,398, July 15, 1943; *C.A.* **38**, 3992 (1944).

3:9102 α,β-**DICHLORO-*n*-BUTYRALDEHYDE** $C_4H_6OCl_2$ Beil. I —
(Crotonaldehyde dichloride; I_1—
2,3-dichlorobutanal-1) I_2-(724)



B.P. 58–60° at 20 mm. (1) **D_4^{21} = 1.2666 (1)** **n_D^{21} = 1.4618 (1)**
48–49° at 13 mm. (2) **D_4^{15} = 1.2716 (1)**

Colorless liq. with odor suggesting chloral. — $\bar{C}$ on exposure to light or on distn. at ord. press. turns brown and decomposes with evoln. of HCl. — $\bar{C}$ is insol. aq.; sol. alc., ether, $CHCl_3$, or CCl_4.

[For prepn. of $\bar{C}$ from crotonaldehyde (1.0150) with Cl_2 directly at −5° (3) cf. (4), or in CCl_4 soln. at 0° (98% yield (1)), or in CS_2 in freezing mixt. (2) see indic. refs.]

$\bar{C}$ with $NaHSO_3$ soln gives (2) a crystn. addn. compound.

[$\bar{C}$ in MeOH contg. 1% HCl gas refluxed 4 hours gives (40% yield (5)) α,β-dichloro-*n*-butyraldehyde dimethylacetal, oil, b p. 86–90° at 13 mm., $D_D^{19.5}$ = 1.179, $n_D^{19.5}$ = 1.4498 (5); note that the presumably corresp behavior of $\bar{C}$ with EtOH and the α,β-dichloro-*n*-butyraldehyde diethylacetal are unreported]

[$\bar{C}$ with ethylene glycol (1:6465) at 100° for 1 hour even in absence of cat. gives (50.3% yield (3)) corresp. cyclic acetal, viz., 2-(α,β-dichloro-*n*-propyl)-1,3-dioxolane, b.p. 100–105° at 13–15 mm. (3).]

[$\bar{C}$ with aq. NaOAc on distn. with steam splits out 1 HCl giving (70–80% yield (6)) (1) (3) (7) α-chlorocrotonaldehyde (3.8117), b.p. 147–150° at 760 mm. (3).]

[$\bar{C}$ with EtMgBr in dry ether followed by usual hydrolysis gives (80% yield (2)) 4,5-dichlorohexanol-3 [Beil. I-439], b.p. 88–93° at 12 mm., D_4^{19} = 1 1685, n_D^{19} = 1.4709 (2). — Similarly, $\bar{C}$ with C_6H_5MgBr gives (66% yield (2)) α,β-dichloro-*n*-propyl-phenyl-carbinol, b.p. 162–168° at 14 mm , D_4^{15} = 1.2355, n_D^{15} = 1.5500 (2)]

[Note that suitable oxidn. of $\bar{C}$ would be expected to yield either or both crotonic acid dichloride (3:1375), m.p. 63°, or isocrotonic acid dichloride (3:1903), m.p. 78°, but that such oxidation has not actually been reported.]

[For use of $\bar{C}$ as component of insecticides see (8).]

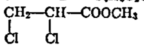
—— α,β-**Dichloro-*n*-butyraldoxime:** oil, not further characterized (2).

—— α,β-**Dichloro-*n*-butyraldehyde phenylhydrazone:** unreported [Note, however, that $\bar{C}$ reacts vigorously with phenylhydrazine (2).]

Ⓓ α,β-**Dichloro-*n*-butyraldehyde semicarbazone:** **m.p. 96–97° (2).**

3:9102 (1) Moureu, Murat, Tampier, *Bull soc. chim.* (4) **29**, 31–32 (1921). (2) Helferich, Besler, *Ber.* **57**, 1277–1278 (1924). (3) Hibbert, Houghton, Taylor, *J. Am. Chem. Soc.* **51**, 613 (1929). (4) Zeisel, *Monatsh.* **7**, 360 (1886). (5) Naftali, *Bull. soc chim.* (5) **4**, 338 (1937). (6) Chattaway, Irving, Outhwaite, *J. Chem Soc.* **1933**, 994 (7) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 351, 137, April 3, 1922; *Cent.* **1922**, IV 155, not in *C.A.* (8) Soc. des Usines Chim. Rhône-Poulenc, Ger. 528, 194, June 26, 1931; *Cent.* **1931**, II 1910, [*C.A.* **25**, 4653 (1931)].

3:9103 METHYL *d,l*-α,β-DICHLOROPROPIONATE $C_4H_6O_2Cl_2$ **Beil. S.N. 162**



B.P. 72–75° at 21 mm. (1)

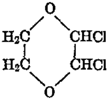
[For prepn. of $\bar{C}$ from technical methyl acrylate (1:3025) in MeOH soln. below 40° by treatment with Cl_2 (85% yield) see (1).]

$\bar{C}$ on distn. with quinoline (2), with dimethylaniline (1), with quinaldine (1), or with other dehydrohalogenating agents (such as Na_2CO_3 (3)) (4) loses HCl giving (73% yield (2)) methyl α-chloroacrylate (3:9096).

$\bar{C}$ on boilg. with 20% HCl hydrolyzes (1) yielding MeOH (1:6120) and α,β-dichloropropionic acid (3:0855) q.v.

3:9103 (1) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940). (2) Marvel, Cowan, *J. Am. C*[illegible]
2,245,547, June 10
(4) Bauer, Lauth

3:9105 2,3-DICHLORODIOXANE $C_4H_6O_2Cl_2$ Beil. S.N. 2668



B.P.	100–101°	at 24–25 mm.	(1)	M.P.	30°	(2)
	97–98°	at 20 mm.	(2)		28–30°	(4) (9)
	88–89°	at 16–17 mm.	(3)			
	85°	at 15 mm.	(4)			
	82°	at 14 mm.	(5)			

$\bar{C}$ is theoretically capable of existing in *cis* and *trans* forms; collateral evidence exists that both may actually be present, but they have not yet been isolated as such.

Although comml. $\bar{C}$ is liq. extremely pure samples may, after inoculation (9), be obtd. in cryst. form.

[For prepn. of $\bar{C}$ from 1,4-dioxane (1:6400) by actn. of Cl_2 at 90° in presence of catalyst such as $SnCl_2$ or I_2 (96 6% yield (6)), or with Cl_2 at 90° for 16 hrs. without catalyst (61% yield (4)), see (6) (4) (7).]

[For studies of further chlorination of $\bar{C}$ see (3) (8); for studies of reaction of $\bar{C}$ with alcohols and phenols see (5) (9) (2) (10) (11) (17); for studies of reaction of $\bar{C}$ with R.MgX cpds. see (12) (13) (4) (14) (15); for reaction of $\bar{C}$ with Mg + I_2 yielding dioxadiene see (16).]

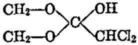
$\bar{C}$ on boiling with aq. for 10 min. gives clear soln. containing hydrolysis products, viz., ethylene glycol (1:6465) and glyoxal. After cooling, making alk., and shaking with BzCl the former can be converted to ethylene glycol dibenzoate (1:2293), extracted with ether, recrystd. from MeOH, m.p. 73° (70–72° (3)); another portion of the aq. soln. of hydrolysis products gives on treatment with *p*-nitrophenylhydrazine hydrochloride a 97% yield of glyoxal-*p*-nitrophenylosazone, yel. cryst., m.p. 306° (310°) (3).

3:9105 (1) Médard, *J. chim. phys.* **33**, 627 (1936). (2) Baker, Shannon, *J. Chem. Soc.* **1933**, 1598. (3) Butler, Cretcher, *J. Am. Chem. Soc.* **54**, 2987–2988 (1932). (4) Summerbell, Bauer, *J. Am. Chem. Soc.* **57**, 2365 (1935). (5) Böeseken, Tellegen, Henriquez, *Rec. trav. chim.* **50**, 909–914 (1931). (6) Kucera, Carpenter, *J. Am. Chem Soc.* **57**, 2346–2347 (1935). (7) Lintner, Scheuer-[illegible]

Soc. **54**, [illegible] *Chem. Soc.* **55**, 4547–4548 (1933). (14) Su[illegible] (15) Summerbell, Umhoefer, *J. Am.* [illegible] hoefer, *J. Am. Chem. Soc.* **61**, 3020–30[illegible] Co.), U.S. 2,069,962, Feb 9, 1937; *C*[illegible] emicals, Inc.), U.S. 2,327,855, Aug. 24, 1943; *C.A.* **38**, 752 (1944).

:9107 β-HYDROXYETHYL DICHLOROACETATE $C_4H_6O_3Cl_2$ (A) Beil. S.N. 160
(2-Hydroxy-2-(dichloromethyl)-1,3-dioxolane) (B) Beil. S.N. 2691

$HOCH_2.CH_2.O.CO.CHCl_2$



(A) (B)

B.P. 106° at 0.08 mm. (1) (3)	D_4^{20} = 1.438 (2)	n_D^{25} = 1.4730 (1)
82° at 0.5 mm. (2)	1.429 (2)	
81–82° at 0.5 mm. (2)		n_D^{23} = 1.4743 (3)
		n_D^{20} = 1.47345 (2)
		1.47253 (2)

Note that C̄ may react either in the acyclic ester form (A) or the dioxolane form (B) .nd doubtless exists as a tautomeric equilibrium of both; in such an equilibrium, however, orm (A) greatly predominates (2); but variations may account for the variation in constants see above).

Colorless oil, spar. sol. aq.—C̄ on long stdg is claimed (2) to disproportionate to ethylene glycol *bis*-(dichloroacetate) (not, however, further described in the literature) and ethylene glycol (1:6465).

[For prepn. of C̄ from ethylene glycol (1.6465) with dichloroacetyl chloride (3:5290) n 1,4-dioxane soln. (75% yield (2)) or from ethylene oxide (1:6105) with dichloroacetic icid (3:6208) (yields: 34% (2), 15% (1)) see indic. refs.]

C̄ on shaking with aq. and simultaneously titrating with $N/10$ aq. NaOH hydrolyzes o ethylene glycol (1:6465) and dichloroacetic acid (3:6208) as shown by Sap. Eq. of 170.8 (2) (calcd. 173).

[C̄ with diazomethane gives not only the methyl ethers of both forms (A) and (B) but also other unexpected products including ethylene glycol (1:6465), ethylene glycol dimethyl ether (1:6141), methyl dichloroacetate (3:5655), etc Note that the methyl ether of structure (B), viz., 2-methoxy-2-(dichloromethyl)-1,3-dioxolane, has b.p 91–92.5° at 9 mm. (2), D_4^{20} = 1.387 (2), n_D^{20} = 1.47032, and is stable to aq. alk.; that corresp. to the acyclic structure (A), viz., β-methoxyethyl dichloroacetate (methyl-" cellosolve " dichloroacetate), best prepared (100% yield (2)) from β-methoxyethanol (1:6405) with dichloroacetyl chloride (3:5290) in $CHCl_3$), has b.p. 55–56° at 0.5 mm. (2), D_4^{20} = 1.309 (2), n_D^{20} = 1.45157 (2).]

3:9107 (1) Allen, Hibbert, *J. Am. Chem. Soc.* **56**, 1399 (1934). (2) Meerwein, Sonke, *J. prakt. Chem.* (2) **137**, 298–301, 311–316 (1933). (3) Hibbert, Greig, *Can J. Research* **4**, 262 (1931).

3:9109 α-CHLORO-*n*-BUTYRALDEHYDE C_4H_7OCl Beil. S.N. 87
(2-Chlorobutanal-1)

$CH_3.CH_2.\underset{\mid \atop Cl}{CH}.CHO$

No record of this compound can be found in the literature. However, for the isomeric β-chloro-*n*-butyraldehyde (3:9110), γ-chloro-*n*-butyraldehyde (3:9111), and α-chloroisobutyraldehyde (3:7235) see indic. refs.

3:9110 β-CHLORO-n-BUTYRALDEHYDE C_4H_7OCl Beil. I —
(3-Chlorobutanal-1) $CH_3.CH(Cl).CH_2.CHO$ I_1—
I_2-(724)

B.P. 28–33° at 13 mm. (1)

[*See also the trimer of* $\bar{C}$ (3:2650).]

Spar. sol. aq. but misc. with org. solvents.
[For prepn. of $\bar{C}$ from crotonaldehyde (1:0150) with 1 mole HCl in ether (50% yield) see (1).]
$\bar{C}$ is difficult to preserve because of rapid polymerization to its trimer, para-β-chloro-n-butyraldehyde (3:2650), m.p. 96–97°. [The product supposed by (2) to have been $\bar{C}$ was actually (1) this trimer.]
[$\bar{C}$ with 3 moles acetaldehyde (1:0100) in the cold gives (53% yield (1)) 2,4-dimethyl-6-(β-chloro-n-propyl)trioxane-1,3,5 [Beil. S.N. 2952], b.p. 83–85° at 13 mm., D_4^{19} = 1.0937, n_D^{19} = 1.4373 (1).]
[$\bar{C}$ with excess EtMgBr yields (1) 5-chlorohexanol-3 [Beil. I_2-(438)] b.p. 78–79° at 13 mm., D_4^{19} = 1.0012, n_D^{19} = 1.4433 (1), together with other products.]
$\bar{C}$ with methylhydrazine in dry ether yields (3) 1,5-dimethylpyrazoline, b.p. 124–132° (picrate, m.p. 112–113° (3)).

3:9110 (1) Helferich, Besler, *Ber.* **57**, 1280 (1924). (2) Kekulé, *Ann.* **162**, 100–102 (1872). (3) von Auwers, Heimke, *Ann.* **458**, 204 (1927).

3:9111 γ-CHLORO-n-BUTYRALDEHYDE C_4H_7OCl Beil. S.N. 87
(4-Chlorobutanal-1) $CH_2(Cl).CH_2.CH_2.CHO$

B.P. 50–51° at 13 mm. (1) $D_{15}^{8.5}$ **= 1.107 (1)** $n_D^{8.5}$ **= 1.44662 (1)**

[For prepn. of $\bar{C}$ from 5-chloropentanediol-1,5 (1) by oxidn with $Pb(OAc)_4$ see (1).]
$\bar{C}$ polymerizes readily on htg. (1).

Ⓓ γ-Chloro-n-butyraldoxime: m.p. 74.5° (1).
Ⓓ γ-Chloro-n-butyraldehyde p-nitrophenylhydrazone: m.p. 110° (1).
Ⓓ γ-Chloro-n-butyraldehyde 2,4-dinitrophenylhydrazone: m.p. 134–135° (1).

3:9111 (1) Paul, *Compt. rend.* **215**, 303–305 (1942); *C.A.* **38**, 4907 (1944).

3:9112 β-CHLORO-ISOBUTYRALDEHYDE C_4H_7OCl Beil. S.N. 87
(3-Chloro-2-methylpropanal-1) $CH_2(Cl)—CH(CH_3)—CHO$

No physical constants for $\bar{C}$ are recorded.
[For prepn. of $\bar{C}$ from 3-chloro-2-methylpropen-2-ol-1 (3:8340) by treatment with acids as specified see (1).]
No other record of $\bar{C}$ appears in the literature.

3:9112 (1) N. V. de Bataafsche Petroleum Maatschappij, French 763,286, April 26, 1934; *Cent.* **1934** II 1531; [*C.A.* **28**, 5077 (1934)].

3:0860 CHLORAL ETHYLALCOHOLATE $C_4H_7O_2Cl_3$ Beil. I - 621
(Chloral alcoholate; trichloroacetaldehyde (mono)ethylacetal) I_1-(330) I_2-(681)

$$Cl_3C.\underset{\displaystyle OH}{\underset{|}{CH}}—OC_2H_5$$

M.P.		B.P.		
[56–57°	(1)]	115–117°		(1)
50°	(2) (3)	116.8°	at 771 mm.	(5)
47.5°	(4)	115–116°		(9)
46.6°	(5)	111.0	at 741.4 mm.	(4)
46°	(6) (7)			
45.2°	(10)			
45°–46.5°	(8)			
40°	(9)			

[*See also chloral* (3:5210) *and chloral hydrate* (3:1270).]

PREPARATION

From chloral. [For prepn. of C̃ from chloral (3:5210) with EtOH (1:6130) (yields: 100% (11), 71.3% with 95% EtOH refluxed 2 hrs (4) (9) (12)) see indic. refs.; for influence of solvents see (13) (14); for formn of C̃ from chloral (3:5210) + *AcH* + *Al*(OEt)$_3$ see (8).]

From chloral hydrate. [For prepn. of C̃ from chloral hydrate (3:1270) with EtOH (1:6130) (yield: 75% in 60 min., 38% in 24 hrs. reflux (4)), with triethyl orthoformate (1:3241) (25% yield in 105 min. reflux (4)), or *with tetraethyl orthosilicate* (4% *yield in* 4 hrs. reflux (4)) see indic. refs.]

From ethyl alcohol. [For formn. of C̃ as end prod. of reaction of ethyl alcohol (1:6130) *with* Cl_2 *see* (15).]

PHYSICAL PROPERTIES

C̃ is less sol. in aq. than chloral hydrate (3:1270) (6) (7). — [For study of toxicity of C̃ as compared with chloral hydrate (3:1270) see (29).]

CHEMICAL BEHAVIOR

Dissociation. C̃ on distillation (7) or in some solns. in org. *solvents cf.* (17) (2) (18) is partially dissociated into chloral (3:5210) and EtOH (1:6130).

Behavior with Inorganic Reactants

With H_2SO_4. C̃ with cold conc. H_2SO_4 yields (1) chloral (3:5210) (or its polymerization products) and $EtHSO_4$.

With aq. alkali. C̃ with aq alkali gives (6) $CHCl_3$ (3:5050) + salts of formic acid (1:1005).

With chlorine. [C̃ with Cl_2 at 80° gives (19) trichloroacetaldehyde diethylacetal (3:6317).]

With PCl_5. [C̃ with PCl_5 in ether below 20° (20) (4) cf. (21) (22) gives (yields: 55–74% (20), 25–33% (11)) α,β,β,β-tetrachloroethyl ethyl ether [Beil. I-623, I_2-(681)], b.p. 189.7° at 758.7 mm. (21), 189.4° at 749.1 mm. cor. (20), 184° at 738 mm. (4), 79° at 16 mm. (20); D_4^{13} = 1.4225 (20).]

Behavior with Organic Reactants

With other alcohols. [C̃ with other alcohols may undergo an exchange of alkyl radicals; for studies of such interchange see (4) (2).]

[For prepn. of C̄ from either the low-boilg. (3:5360) or high-boilg. (3:5615) stereoisomers of 1,2-dichlorobutene-2 (together with 2-chlorobutene-2-ol-1 (3:8240)) by hydrolysis with 2 pts. aq + 1 mole $CaCO_3$ for 4 hrs. at 70° see (1); note that C̄ is formed by virtue of allylic transposition during the process and that *Cent.* and *C.A.* do not agree on the boilg. pt. (orig. inaccessible).

Ⓓ 3-Chlorobuten-3-yl-2 *N*-(α-naphthyl)carbamate: m.p. 92–92.5° (1).

3:9115 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 658–662 (1937); *Cent.* **1937**, II 371; *C.A.* **31**, 5754 (1937).

3:9130 *d,l*-α-CHLORO-*n*-BUTYRIC ACID $C_4H_7O_2Cl$ Beil. II - 276

II₁-(123)

II₂-(253)

$$\begin{array}{l}CH_3\text{—}CH_2.\underset{\displaystyle |\atop \displaystyle Cl}{C}H.COOH\end{array}$$

B.P. 109.5° at 24 mm. (1) $D_4^{20} = 1.1796$ (13) $n_D^{20} = 1.4411$ (13)

101.25° at 15 mm. (2)

Viscous liq.; spar. sol. cold aq.; eas. sol. hot aq.

[For prepn. of C̄ from diethyl α-ethyl-α-chloromalonate by hydrolysis and subsequent htg. of the resultant α-ethyl-α-chloromalonic acid (90% yield (1)) (2) see indic. refs.; from *n*-butyric acid (1:1035) with SO_2Cl_2 + acetyl chloride (3:7065) (3) or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (10% C̄ + 45% β- (3:0035) and 45% γ- (3:0020) isomers) see (4); from *n*-butyric acid with Cl_2 and suitable cat. see (5); from α-chloro-*n*-butyryl chloride (3:5570) by hydrolysis with aq. see (7).]

C̄ with $SOCl_2$ (1) yields α-chloro-*n*-butyryl chloride (3:5570), b.p. 129–132°.

[C̄ (in the form of $Ca\bar{A}_2$) on cat. hydrogenation with $Pd/BaSO_4$ in aq. alc. is completely converted (6) to *n*-butyric acid; C̄ itself is only partially (6) reduced.]

[For study of rate of hydrolysis of the halogen in NaĀ by aq. at 70° see (8).]

—— Methyl *d,l*-α-chloro-*n*-butyrate: b.p. 145–146° at 756 mm. (See 3:8103.)

—— Ethyl *d,l*-α-chloro-*n*-butyrate: b.p. 163–164° at 760 mm. (See 3:8307.) For study of rate of esterification of C̄ with EtOH see (9).]

Ⓓ *d,l*-α-Chloro-*n*-butyramide: cryst. from C_6H_6, m.p. 81° (10), 78.4–78.9° (11). [From methyl α-chloro-*n*-butyrate (3:8103) with conc. aq. NH_4OH (60% yield (10)).]

Ⓓ *d,l*-α-Chloro-*n*-butyranilide: m.p. not reported. [From α-chloro-*n*-butyryl chloride (3:5570) with aniline (1).]

Ⓓ *d,l*-α-Chloro-*n*-butyro-*p*-toluidide: m.p. 98° (12).

3:9130 (1) Blaise, *Bull soc. chim.* (4) **15**, 668 (1914). (2) Cloves, *Ann.* **319**, 357–358 (1901). (3) Blank, Ger. 157,816, Jan 18, 1905; *Cent.* **1905**, I 414. (4) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (5) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; *Cent.* **1936**, I 880; *C.A.* **29**, 6608 (1935). (6) Paal, Schiedewitz, *Ber.* **62**, 1937–1938 (1929). (7) Markownikow, *Ann.* **153**, 241 (1870). (8) Simpson, *J. Am. Chem. Soc.* **40**, 679 (1918). (9) Lichty, *Ann.* **319**, 372 (1901). (10) De Boosere, *Bull. soc chim. Belg.* **32**, 44–45 (1923).
(11) Vandewijer, *Bull. soc. chim. Belg.* **45**, 255 (1936). (12) Wolffenstein, Rolle, *Ber*, **41**, 736 (1908). (13) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

—— *d,l*-β-CHLORO-*n*-BUTYRIC ACID $C_4H_7O_2Cl$ Beil. II - 277

II₁-(123)

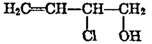
II₂-(253)

$$CH_3\text{—}\underset{\displaystyle |\atop \displaystyle Cl}{C}H.CH_2.COOH$$

B.P. 116° at 22 mm. M.P. 16–16.5° $D_4^{20} = 1.1898$ $n_D^{20} = 1.4421$

See 3:0035. *Division A: Solids.*

3:9113 *d,l*-**2-CHLOROBUTEN-3-OL-1** C_4H_7OCl Beil. S.N. 25



B.P. 69.5–70.0° at 30 mm. (1) (2) n_D^{20} **= 1.4665 (1) (2)**
66.5–67.0° at 30 mm. (3)

[*See also* 1-*chlorobuten*-3-*ol*-2 (3:8110).]

[For prepn. of C̄ from 3,4-epoxybutene-1 (1) (2) with conc. HCl (2 moles) in ether below 5° (61% yield (2)) or with cold conc. HCl (60% yield (3)) see indic. refs.; note that by these methods C̄ is accompanied by a small amt. (2% (2)) of 4-chlorobuten-2-ol-1 (1-chlorobuten-2-ol-4) (3:9114).]

C̄ with Br_2 gives (3) 2-chloro-3,4-dibromobutanol-1, b.p. 133.5–135.5° at 10 mm. (3).

C̄ with KOH (3) loses HCl, ring-closing to 3,4-epoxybutene-1, b.p. 67° at 750 mm. (3), 65.0–65.8° at 739 mm. (2); D_4^{20} = 0.8745 (2) (3); n_D^{20} = 1.4170 (2) cf. (3).

[For study of hydrolysis of C̄ with aq. NaOH see (1).]

—— **2-Methoxybuten-3-ol-1** (C̄ methyl ether): b.p. 70° at 50 mm. (2); n_D^{20} = 1.4290 (2): corresp. 3,5-dinitrobenzoate, m.p. 68–71° (2). [From C̄ with MeOH/NaOMe refluxed 30 min. (52% yield (2))]

—— **1-Chlorobuten-3-yl-1 acetate**: b.p. 79.5–80° at 30 mm. (3). [Note that with KOH this prod. loses AcOH, ring-closing (3) to 3,4 epoxybutene-1 (above).]

—— **1-Chlorobuten-3-yl-1 3,5-dinitrobenzoate**: m.p 65.6° u.c. (2). [Note that this prod. depresses m.p. of corresp. deriv. (m p. 61.5–63.5° u.c.) from 1-chlorobuten-3-ol-2 (3:8110).]

3:9113 (1) Kadesch, *J. Am. Chem. Soc.* **68**, 46–48 (1946) (2) Kadesch, *J. Am. Chem Soc.* **68**, 41–45 (1946). (3) Petrov, *J. Gen. Chem.* (*U.S S R.*) **11**, 991–995 (1941); *C.A.* **37**, 1699 (1943).

3:9114 4-CHLOROBUTEN-2-OL-1 C_4H_7OCl Beil. S.N. 25
(1-Chlorobuten-2-ol-4)

B.P. 67–69° at 4–5 mm. (2) $n_D^{20.5}$ **= 1.4792 (1)**
64–65° at 2 mm. (2)
54–55° at 2 mm. (1) n_D^{20} **= 1.4845 (2)**

[For form. of C̄ in small amount (18.6% yield (2)) from 3,4-epoxybutene-1 with HCl see (1) (2); note that the main product of this reaction is 2-chlorobuten-3-ol-1 (3:9113) (1) (2).]

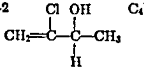
[For study of hydrolysis of C̄ with aq or aq. NaOH see (2).]

—— **4-Chlorobuten-2-yl-1 3,5-dinitrobenzoate**: unreported.

Ⓓ **4-Chlorobuten-2-yl-1** ***N*-(α-naphthyl)carbamate**: m.p. 88–89° (1).

3:9114 (1) Kadesch, *J. Am Chem. Soc.* **68**, 45 (1946). (2) Kadesch, *J. Am. Chem. Soc.* **68**, 46–48 (1946)

3:9115 *d,l*-**3-CHLOROBUTEN-3-OL-2** C_4H_7OCl Beil. S.N. 25



B.P. 53–57° at 19 mm. (1) D_4^{23} **= 1.1138 (1)** n_C^{23} **= 1.46232 (1)**
67–68° at 19 mm. (1)

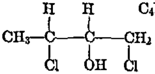
Colorless liq. insol. aq.

[For prepn. (93% yield (1)) from β-methoxyethanol (methyl "cellosolve") (1:6405) + phosgene (3:5000) see (1).]

Ⓓ β-Methoxyethyl carbamate: from C̄ + aq. NH_4OH in poor yield (13.3% (1)); m.p. 46.8° (1).

3:9140 (1) Ashburn, Collett, Lazzell, *J. Am. Chem. Soc.* **60**, 2933–2934 (1938).

3:9145 1,3-DICHLOROBUTANOL-2



$C_4H_8OCl_2$ Beil. I-373
I_1—
I_2—

B.P. 63–64° at 10 mm. (1) D_4^{15} = 1.2870 (1) n_D^{20} = 1.4766 (1) n_D^{15} = 1.4790 (1)

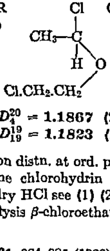
[For prepn. of C̄ from 3-chloro-1,2-epoxybutane (α-chloroethylethylene oxide) or from 1-chloro-2,3-epoxybutane (α-(chloromethyl)-α′-methylethylene oxide) by addn. of HCl see (1); for possibly similar processes cf. (2).]

C̄ on oxidn. gives (1) 1,3-dichlorobutanone-2 (3:5900).

—— 1,3-Dichloro-*sec.*-butyl acetate: b.p. 82.5–83.5° at 10 mm., D_4^{20} = 1.2185, D_4^{15} = 1.2229; n_D^{20} = 1.4530, n_D^{15} = 1.4550 (1).

3:9145 (1) Petrov, *J. Am. Chem. (U.S.S.R.)* **11**, 713–721 (1941); *Cent.* **1942**, I 2867; *C.A.* **36**, 404 (1942). (2) Zikes, *Monatsh.* **6**, 348–355 (1885).

3:9150 α,β′-DICHLORODIETHYL ETHER
(α-Chloroethyl-β-chloroethyl ether)



$C_4H_8OCl_2$ Beil. I —
I_1—
I_2-(674)

B.P. 55–57° at 17 mm. (1)
51° at 10 mm. (2)

D_4^{20} = 1.1867 (2) n_D^{20} = 1.4473 (2)
D_{19}^{19} = 1.1823 (1) $n_D^{16.2}$ = 1.4497 (1)

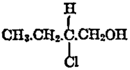
Colorless liq. fumg. in air and decomposing on distn. at ord. press. (1).

[For prepn. (60% yield (2)) from ethylene chlorohydrin (3:5552) + acetaldehyde (1:0100) (2) or paraldehyde (1:0170) (1) + dry HCl see (1) (2).]

C̄ rapidly dis. in cold aq. yielding by hydrolysis β-chloroethanol (3:5552), acetaldehyde (1:0100), and HCl (1).

3:9150 (1) Grignard, Purdy, *Bull. soc. chim.* (4) **31**, 984–985 (1922). (2) Lingo, Henze, *J. Am. Chem. Soc.* **61**, 1574–1575 (1939).

3:9160 2-CHLOROBUTANOL-1
(β-Chloro-*n*-butyl alcohol)

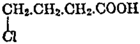


C_4H_9OCl Beil. S.N. 24

B.P. 74–76° at 25 mm. (1) D_4^{25} = 1.062 (1) n_D^{25} = 1.4410 (1)

[For prepn. of C̄ (83% yield (1)) by saponification of the corresp. trichloroacetate obtd. by chlorination of *n*-butyl trichloroacetate (3:6315) see (1).]

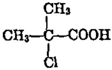
—— γ-CHLORO-n-BUTYRIC ACID $C_4H_7O_2Cl$ Beil. II - 278; II_1-(124); II_2-(253)



B.P. 196° at 22 mm. **M.P. 16°** D_4^{20} = **1.2236** n_D^{20} = **1.4512**

See 3:0020. *Division A: Solids.*

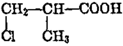
—— α-CHLORO-ISOBUTYRIC ACID $C_4H_7O_2Cl$ Beil. II-294; II_1—; II_2—



B.P. 118° at 60 mm. **M.P. 31°**

See 3:0235. *Division A: Solids.*

3:9132 β-CHLORO-ISOBUTYRIC ACID $C_4H_7O_2Cl$ **Beil. S.N. 162**



B.P. 128–133° at 60 mm. (1)

[For prepn. of $\bar{C}$ from isobutyric acid (1:1030) with Cl_2 in pres. of S (2) (3) or in activating light (1) (note that some α-chloro-isobutyric acid (3:0235) is also formed) see indic. refs.; for prepn. of $\bar{C}$ from isobutyric acid (1:1030) with SO_2Cl_2 in presence of dibenzoyl peroxide in CCl_4 soln. (85% yield $\bar{C}$ + 15% α-isomer) see (4).]

$\bar{C}$ should by conventional means such as $SOCl_2$, etc., be convertible to the corresp. β-chloroisobutyryl chloride (3:9101), but no record of such transformation appears in the literature, the expected product having been prepd. by indirect means.

- —— Methyl β-chloroisobutyrate: b.p. 151–155° at 750 mm., 85–90° at 60 mm., D_{15}^{15} = 1.1101 n_D^{15} = 1.4297 (1). [From $\bar{C}$ in MeOH with H_2SO_4 in 70% yield (1) cf. (3); note that this prod. on htg. with quinoline (1) or passing over hot silica gel (3) loses HCl giving (87% yield (1)) methyl methacrylate.]
- —— Ethyl β-chloroisobutyrate: b.p. 56–58° at 10 mm. (5). [From ethyl β-hydroxy-isobutyrate with PCl_5 in dry ether (40% yield (5)).]
- —— β-Chloroisobutyramide: unreported.
- —— β-Chloroisobutyranilide: m.p. 109.0–109.5° (4), 104–105° (6).
- —— β-Chloroisobutyr-p-toluidide: unreported.

–1044 (1937), *Cent.* 1938, II
: acid has been erroneously
oisooleic acid" throughout.
(2) Loder, Ries (to du Pont Co.), U.S. 2,043,670, June 9, 1936, *Cent.* 1936, II 2229, *C.A.* 30, 5240 (1936). (3) Loder (to du Pont Co.), Brit. 428,223, June 6, 1935; *Cent.* 1936, I 179; *C.A.* 29, 6607 (1935). (4) Kharasch, Brown, *J. Am. Chem. Soc.* 62, 925–929 (1940). (5) Rydon, *J. Chem. Soc.* 1936, 1448. (6) Michael, Garner, *Ber.* 34, 4054–4055 (1901).

3:9140 β-METHOXYETHYL CHLOROFORMATE $C_4H_7O_3Cl$ **Beil. S.N. 199**
(Methyl "cellosolve" chloroformate; β-methoxyethyl chlorocarbonate) $CH_3.O.CH_2.CH_2.O.CO.Cl$

B.P. 58.7° at 13 mm. (1) D^{25} ...

(3) (4) (8)) see (3) (4) (8); from tetramethylene glycol (1:6516) with $SOCl_2$ + pyridine (47% yield (1)) or S_2Cl_2 (2) see (1) (2); from δ-chlorobutyl acetate by alcoholysis with MeOH (80% yield) see (6); for mfg. from ethylene oxide + C_2H_5Cl + $AlCl_3$ (or other catalysts) see (9).]

C̄ (2 moles) treated with PBr_3 (1 mole) gives (98% yield (3)) tetramethylene chlorobromide, b.p. 175–176°, D_4^{20} = 1.488, n_D^{20} = 1.4885 (3). [For study of reaction of C̄ with HBr see (7).]

—— δ-Chloro-*n*-butyl acetate: oil, b.p. 92–93° at 22 mm. (6), 92–94° at 22 mm. (10); D_4^{20} = 1.0805 (6); n_D^{20} = 1.43439 (6). [From tetrahydrofuran [Beil. XVII-10] with AcCl (6) as directed cf. (10) or with AcOH + HCl + cat. (11).]

—— δ-Chloro-*n*-butyl benzoate: oil, b.p. 140–142.5° at 4 mm., D_4^{20} = 1.1429, n_D^{20} = 1.52028 (6). [From tetrahydrofuran [Beil. XVII-10] with benzoyl chloride + $ZnCl_2$ (54.5% yield (6)).]

—— δ-Chloro-*n*-butyl *p*-nitrobenzoate: oil, b.p. 205–206° at 7 mm. (12). [From tetrahydrofuran [Beil. XVII-10] with *p*-nitrobenzoyl chloride + $SnCl_2$ (12).]

—— δ-Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.

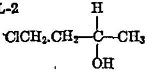
Ⓓ δ-Chlorobutyl *N*-phenylcarbamate: cryst. from pet. eth. (1); m.p. 54° (1), 54–55° (5).

Ⓓ δ-Chlorobutyl *N*-(α-naphthyl)carbamate: cryst. from pet. eth. (1); m.p. 69–70° (1), 69° (3); 66° (2).

3:9170 (1) Kirner, Richter, *J. Am. Chem. Soc.* **51**, 2505–2506 (1929). (2) Bennett, Heathcoat, *J. Chem. Soc.* **1929**, 272. (3) Starr, Hixon, *J. Am. Chem. Soc.* **56**, 1595–1596 (1934). (4) Starr, Hixon, *Org. Syntheses*, Coll. Vol. **2** (1st ed.), 571–572 (1943). (5) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3363 (1939). (6) Cloke, Pilgrim, *J. Am. Chem. Soc.* **61**, 2667–2669 (1939). (7) Bennett, Reynolds, *J. Chem. Soc.* **1935**, 139. (8) Yur'ev, Minacher, Samurskaya, *J. Gen.Chem.* (*U.S.S.R.*) **9**, 1710–1716 (1939); *C.A.* **34**, 3731 (1940). (9) I.G., Brit. 354,992, Sept. 10, 1931; *Cent.* **1931**, II 3545. (10) Manchen, Schmidt (to I.G.), Ger. 736,428, May 6, 1943; *C.A.* **38**, 2966 (1944): U.S. 2,314,454, March 23, 1943; *C.A.* **37**, 5078 (1943).

(11) Seidenfaden, Bröker (to I.G.), Ger. 725,528, Aug. 13, 1942; *C.A.* **37**, 5985 (1943). (12) Smorgonskii, Gold'farb, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 1113–1119 (1940); *C.A.* **35**, 4011 (1941).

3:9175 *d,l*-4-CHLOROBUTANOL-2 (1-Chlorobutanol-3) C_4H_9OCl Beil. I — I_1-(188) I_2—



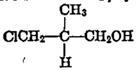
B.P. 70° at 13 mm. (1)

[For prepn. from 3-chloropropanal-1 (β-chloropropionaldehyde) (3:5576) + CH_3MgI see (1) (2).]

[4-Phthalimidobutanol-2, cryst. from pet. eth., m.p. 47–48°, although never recorded by reactn. of C̄ with K phthalimide, has been prepd. indirectly (3).]

3:9175 (1) Fourneau, Ramart-Lucas, *Bull. soc. chim.* (4) **25**, 367 (1919). (2) Backer, Bilt, *Rec. trav. chim.* **54**, 69–70 (1935). (3) Robinson, Suginome, *J. Chem. Soc.* **1932**, 308.

3:9180 3-CHLORO-2-METHYLPROPANOL-1 C_4H_9OCl Beil. S.N. 24



B.P. 76–78° at 21 mm. (1) D_4^{25} = 1.083 (1) n_D^{25} = 1.4460 (1)

C̄ with $SOCl_2$ + pyridine gives (1) 1,2-dichlorobutane (3:7680), b.p. 127°, n_D^{25} = 1.4420 (1).

—— β-Chloro-*n*-butyl acetate: unreported.
—— β-Chloro-*n*-butyl benzoate: unreported.
—— β-Chloro-*n*-butyl *p*-nitrobenzoate: unreported.
—— β-Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.
Ⓓ β-Chloro-*n*-butyl *N*-phenylcarbamate: m.p. 52.5–53.5° (1).
—— 2-(*N*-Phthalimino)butanol-1: unreported.

3:9160 (1) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3363 (1939).

3:9165 3-CHLOROBUTANOL-1 C_4H_9OCl **Beil. S.N. 24**
(γ-Chloro-*n*-butyl alcohol)

$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2.CH_2OH$$

B.P. 67–68° at 15 mm. (1) D_4^{20} = **1.06218 (1)** n_D^{20} = **1.44464 (1)**
61° at 10 mm. (2)

C̄ on distn. at atm. press. or on htg. with quinoline loses HCl and yields crotonyl alc. $CH_3.CH{=}CH.CH_2OH$, b.p. 120–121° at 755 mm., D_4^{20} = 0.85306, n_D^{20} = 1.42976 (*N*-phenylcarbamate, m.p. 79.4–80°) (1).

[For prepn. of C̄ from butanediol-1,3 (1:6482) + HCl see (1) (3); from γ-chloro-*n*-butyl butyrate by hydrol. with HCl see (2); from C_3H_6 + 30% CH_2O + HCl at 50° see (4).]

[C̄ over Al_2O_3 at 250° gives (3) butadiene-1,3.]

—— γ-Chloro-*n*-butyl acetate: unreported.
—— γ-Chloro-*n*-butyl benzoate: unreported.
—— γ-Chloro-*n*-butyl *p*-nitrobenzoate: unreported.
—— γ-Chloro-*n*-butyl 3,5-dinitrobenzoate: unreported.
—— γ-Chloro-*n*-butyl *N*-phenylcarbamate: unreported.
—— 3-(*N*-Phthalimino)butanol-1: unreported.

3:9165 (1) Verhulst, *Bull. soc. chim. Belg* **40**, 85–90 (1931). (2) Heyse (to I.G.), Ger. 524,435, May 7, 1931; *Cent* **1931**, II 767. (3) Runge, Muller-Cunradi (to I.G.), Ger. 578,038, June 12, 1933, *Cent* **1933**, II 935. (4) I.G , Brit. 465,467, June 3, 1937, *Cent.* **1937**, II 1445.

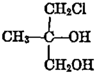
3:9170 4-CHLOROBUTANOL-1 C_4H_9OCl **Beil. I —**
(δ-Chloro-*n*-butyl alcohol; $ClCH_2.CH_2.CH_2.CH_2.OH$ **I_1—**
tetramethylene chlorohydrin) **I_2-(398)**

B.P. 84–85° at 16 mm. (1)	D_4^{25} = **1.125 (5)**	n_D^{25} = **1.4551 (5)**
86° at 15 mm. (2)	D_4^{20} = **1.0883 (1)**	n_D^{20} = **1.4518 (1)**
81–82° at 14 mm. (3) (4)	**1.0867 (8)**	**1.4529 (8)**
72–75° at 10 mm. (5)		
70–71° at 7 mm. (4)		
64–65° at 3 mm. (6)		
57° at 0.5 mm. (7)		

Colorless liq. — On distn. above 16 mm. splits off HCl (1) (2) yielding tetrahydrofuran, b.p. 63°.

[For prepn. from tetrahydrofuran [Beil. XVII-10] by actn. of HCl gas (yield; 54–57%

3:9190 d,l-3-CHLORO-2-METHYLPROPANEDIOL-1,2 $C_4H_9O_2Cl$ **Beil. S.N. 30**
(β-Methylglycerol-α-monochlorohydrin)



B.P. 80° at 1.6 mm. (1) D_4^{20} **= 1.2362 (1)** n_D^{20} **= 1.4748 (1)**

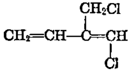
Colorless viscous liq., misc. in all proportions with aq., alc., ether (1).

[For prepn. of C̄ from 1-chloro-2-methyl-2,3-epoxypropane ("β-methylepichlorohydrin") (3:7657) by warming with 0.1% aq. H_2SO_4 (95% yield (1)) see (1) (2).]

C̄ with aq. 15% NaOH at 10–20° reacts very rapidly (by loss of HCl and ring closure) giving (70% yield (1)) (3) by ether extraction 2,3-epoxy-2-methylpropanol-1 (β-methylglycidol), colorless liq. misc. with aq., alc., or ether, b.p. 68° at 25 mm., D_4^{20} = 1.0420, n_D^{20} = 1.4299 (1). [This prod. on further hydration in the aq. soln. yields 2-methylpropanetriol-1,2,3 (β-methylglycerol), b.p. 115–120° at 1.6 mm., D_4^{20} = 1.1863, n_D^{20} = 1.4730 (1).]

3:9190 (1) Hearne, DeJong, *Ind. Eng. Chem.* **33**, 940–943 (1941). (2) Groll, Hearne (to Shell Development Co.), U.S. 2,086,077, July 6, 1937; *Cent.* **1937**, II 2433; *C.A.* **31**, 5813 (1937). (3) Groll, Hearne (to Shell Development Co), U.S. 2,070,990, Feb. 16, 1937; *Cent.* **1937**, II 2433; *C.A.* **31**, 2612 (1937).

3:9195 1-CHLORO-2-(CHLOROMETHYL)BUTADIENE-1,3 $C_5H_6Cl_2$ **Beil. I —**
I_1—
I_2—



No physical constants on C̄ are cited by the abstract journals.

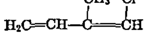
[For formn. of C̄ from 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230) with boilg. alc. KOH (2-(chloromethyl)-1,3-dichlorobutene-1 (3:9201) is also formed) see (1).]

C̄ readily polymerizes (1).

C̄ with maleic anhydride (1:0625) forms addn. prods. (1).

3:9195 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936); *Cent.* **1937**, I 573; *C.A.* **31**, 1003 (1937).

3:9200 1-CHLORO-2-METHYLBUTADIENE-1,3 C_5H_7Cl **Beil. S.N. 12**
("Isoprene monochloride")



B.P. 50.4° at 100 mm. (1) D_4^{20} **= 0.9710 (1)** n_D^{20} **= 1.4792 (1)**

C̄ has pleasant odor resembling isoprene.

[For prepn. of C̄ (38% yield (1) together with other products) from 2-methylbutadiene-1,3 (isoprene) with Cl_2 in CCl_4 see (1); for formn. of C̄ (30% yield (2) together with other products) from 1,2,3-trichloro-2-methylbutane (3:6100) with 2 moles of quinoline at 185–225° see (2).]

C̄ with 4 pts. liq. SO_2 gives (1) 1-chloro-2-methylbutene-2 1,4-sulfone, white rhombic plates from water (which effectively separates the accompanying tar), or from ether, m.p. 73° cor. (1). [This prod. is a potent sternutator and skin irritant; its soly. in aq. is about

[For prepn. (76% yield (1)) via hydrolysis of the corresp. trichloroacetate (obtd. by chlorination of isobutyl trichloroacetate) see (1).]

Ⓓ β-Chloro-α-methyl-*n*-propyl *N*-phenylcarbamate: m.p. 63.5–64° (1).

3:9180 (1) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3363 (1939).

3:9185 2-(β-CHLOROETHOXY)ETHANOL-1 $C_4H_9O_2Cl$ **Beil. I - 467**
(Diethylene glycol chlorohydrin; ethylene glycol mono-β-chloroethyl ether; β-chloroethyl β-hydroxyethyl ether; β-chloro-β′-hydroxydiethyl ether)

$$\underset{\displaystyle Cl}{\underset{|}{CH_2}}—CH_2—O—CH_2—CH_2OH$$

I_1—
I_2-(519)

B.P. 180–185°		(1)
92–100°	**at 12 mm.**	(2)
93–96°	**at 11 mm.**	(3)

Colorless mobile highly refractive liq. — Very sol. aq. but can be salted out by addition of K_2CO_3. — Misc. with alc. or ether. [For study of toxicity see (11).]

[For prepn. of C̄ from ethylene chlorohydrin (3:5552) with ethylene oxide (1:6105) at 140° (4) in pres. of $SnCl_4$, $AlCl_3$, etc. (2), or acidified hydrosilicate cat. (3), or conc. H_2SO_4 (30–35% yield (5)) (together with numerous other prods.), or with ethylene glycol (1:6465) + HCl gas as directed (1) see indic. refs.; for prepn. from ethylene oxide (1:6105) satd. with HCl gas see (4); for formn. of C̄ during extractn. of lignin from pine wood by means of ethylene chlorohydrin + HCl see (6).]

[For use of quat. salts obtd. from C̄ by treatment with oleic acid followed by pyridine or from C̄ with *n*-octadecylamine followed by pyridine and chloroacetic acid see (7); for use of C̄ as rat poison see (8).]

[C̄ with hot aq. alk. ring-closes with loss of HCl giving (90–95% yield (9)) 1,4-dioxane (1:6400).]

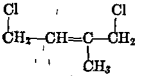
[C̄ (1 mole) with Me_2NH (3 moles) in C_6H_6 in s.t. at 120° for 8 hrs. gives (75% yield (5)) 2-(β-dimethylaminoethoxy)ethanol-1, b.p. 95° at 15 mm. (B̄.picrolonate, m.p. 110°; B̄.*m*-nitrobenzoate.HCl, m.p. 142°) (5).]

—— 2-(β-Chloroethoxy)ethyl acetate: oil, b.p. 94–95° at 11 mm. (6).

—— 2-(β-Chloroethoxy)ethyl *p*-toluenesulfonate: oil; consts. not reported. [From C̄ (1 mole) with *p*-toluenesulfonyl chloride (0.75 mole) at 142° for 10 hrs. (yield 59% (10)); for use in introduction of 2-(β-chloroethoxyethyl) group see (10).]

3:9185 (1) Lourenco, *Ann. chim.* (3) **67**, 290–292 (1863). (2) Haussmann, Götz, Ger. 670,419, Jan 18, 1939; *Cent.* **1939**, II 560; *C.A.* **33**, 3031 (1939). (3) I.G., Brit. 354,357, Sept. 3, 1931; *Cent.* **1931**, II 2657; *C.A.* **26**, 3885 (1932). (4) Wurtz, *Ann. chim* (3) **69**, 338–341 (1863). (5) Fourneau, Ribas, *Bull. soc. chim.* (4) **41**, 1046–1051 (1927). (6) Freudenberg, Acker, *Ber.* **74**, 1400 (1941). (7) I.G., Brit. 474,671, Dec. 2, 1937; *Cent.* **1938**, 2063, *C.A.* **32**, 3518 (1938); French 819,000, Oct. 7, 1937; *Cent.* **1938**, 2063; *C.A.* **32**, 2653 (1938) (8) I.G., Brit. 474,677, Dec. 2, 1937; *Cent.* **1938**, I 2045; *C.A.* **32**, 3064 (1938); French 805,557, Nov. 24, 1936; *Cent* **1937**, I 3397; *C.A.* **31**, 4417 (1937). (9) Webel (to I G), Ger. 520,478, Oct. 8, 1932; *Cent.* **1933**, I 1019; *C.A.* **27**, 737 (1933). (10) Butler, Renfrew, Cretcher, Souther, *J. Am. Chem. Soc.* **59**, 228–229 (1937).
(11) Smyth, Carpenter, *J. Ind. Hyg. Toxicol.* **26**, 269–273 (1944).

3:9204 1,4-DICHLORO-2-METHYLBUTENE-2 $C_5H_8Cl_2$ Beil. S.N. 11



B.P. 93° at 50 mm. (1) $D_4^{20} = 1.1526$ (1) $n_D^{20} = 1.4932$ (1)
56° at 10 mm. (1)

Colorless lachrymatory liquid. — Sol. in cold conc. H_2SO_4 with yel.-br. color.

[For prepn. from 2-methylbutadiene-1,3 (isoprene) (1:8020) in CCl_4 by treatment with Cl_2 see (1) (1-chloro-2-methylbutadiene-1,3 (3:9200) is also formed (1)).]

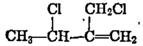
$\bar{C}$ in alc. added dropwise to a suspension of Zn dust in hot alc. gives (77% yield (1)) 2-methylbutadiene-1,3 (isoprene) (1:8020), b.p. 34°.

$\bar{C}$ on oxidn. with $KMnO_4$ in acetone at −5° gives (1) 1,4-dichloro-2-methylbutanediol-2,3, ndls. from ether, m.p. 106.5° cor. (1).

$\bar{C}$ in $CHCl_3$ treated with O_3, then with aq., yields (1) chloroacetone (3:5425) and chloroacetaldehyde (3:7212); ozonolysis of $\bar{C}$ without solvent followed by $KMnO_4$ oxidn. gives (1) chloroacetic acid (3:1370).

3:9204 (1) Jones, Williams, *J. Chem. Soc.* **1934**, 829–834.

3:9206 *d,l*-3-CHLORO-2-(CHLOROMETHYL)BUTENE-1 $C_5H_8Cl_2$ Beil. S.N. 11



B.P. 39–40° at 7 mm. (1) $D_4^{18} = 1.1328$ (1) $n_C^{18} = 1.4713$ (1)

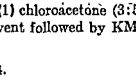
[For formn. of $\bar{C}$ from 3-chloro-2-methylbutene-1 (3:7300) with Cl_2 + $NaHCO_3$ at 0° see (1) (yield of $\bar{C}$ is 35% accompanied by 30% 1,3-dichloro-2-methylbutene-2 (3:8170) and 30% 1,2,3-trichloro-2-methylbutane (3:6100)) (1).]

$\bar{C}$ upon ozonolysis yields (1) 1,3-dichlorobutanone-2 (3:5900).

3:9206 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939).

—— 1,3-DICHLORO-2,2-*bis*-(CHLOROMETHYL)PROPANE $C_5H_8Cl_4$ Beil. I - 141

I_1—
I_2-(104)



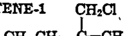
B.P. 110° at 12 mm. M.P. 97°

See 3:2675. Division A: Solids.

3:9214 2-(CHLOROMETHYL)BUTENE-1 C_5H_9Cl Beil. I - 211

(β-Ethylallyl chloride)

I_1—
I_2-(187)



$\bar{C}$ has not been obtd. in pure form.

[For formn. of $\bar{C}$ together with 1-chloro-2-methylbutene-1 (3:7303) + 1-chloro-2-methylbutene-2 (3:7485) from 1-chloro-2-methylbutanol-2 (3:8175) by distn. with anhydrous

2.4 g. at 15° and 7.2 g. per 100 ml. aq.; in boilg. aq. it gives a tar, and aq. solns. are therefore concd. under reduced press.; on htg. to 140° under 100 mm. press. it regenerates (77% yield) $\bar{C}$ and thus constitutes a convenient means for storing $\bar{C}$ in stable form. (1).]

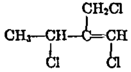
$\bar{C}$ polymerizes at a rate comparable to that of isoprene (for details see (1)).

$\bar{C}$ (6 g.) + 1,4-naphthoquinone (1:9040) (3.5 g.) htd. under N_2 for 4 hrs. at 80° gives (1) on cooling 1-chloro-2-methyltetrahydroanthraquinone, pale yel. ndls. from acetone, colorless ndls. from alc., m.p. 146° cor. (1); this prod. on oxidn. with air in alc. NaOH yields 1-chloro-2-methylanthraquinone, cryst. from AcOH or alc., m.p. 171–172° cor. (1) (3) [dif. from 3-chloropentadiene-1,3 (3:7360) q.v.].

$\bar{C}$ with maleic anhydride (1:0625) evolves HCl and yields (2) a dianhydride.

3:9200 (1) Jones, Williams, *J. Chem. Soc.* **1934**, 829–835. (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **6**, 1116–1132 (1936); *Cent.* **1937**, I 573, *C.A.* **31**, 1003 (1937). (3) Keimatsu, Hirano, *J. Pharm. Soc. Japan*, **49**, 140–147 (1929), *C.A.* **23**, 3466 (1929).

3:9201 2-(CHLOROMETHYL)-1,3-DICHLOROBUTENE-1 $C_5H_7Cl_3$ Beil. S.N. 11



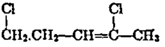
B.P. 77–84° at 15 mm. (1) D_4^{12} = **1.33** (1) n_C^{12} = **1.4975** (1)

[For prepn. of $\bar{C}$ from 2-(chloromethyl)1,2,3-trichlorobutane (3:5230) by loss of HCl with boilg. alc. KOH (1-chloro-2-(chloromethyl)butadiene-1,3 (3:9195) is also formed) see (2); for formn. of $\bar{C}$ from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with Cl_2 + $NaHCO_3$ at 0° (yield 6% $\bar{C}$ together with 90% 2-(chloromethyl)-1,2,3-trichlorobutane (3:5230)) see (1).]

$\bar{C}$ on ozonolysis yields (2) 1,3-dichlorobutanone-2 (3:5900) and formic acid (1:1005).

3:9201 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939). (2) Tishchenko. *J. Gen. Chem. (U.S.S.R.)* **6**, 1116–1132 (1936); *Cent.* **1937**, I 573; *C.A.* **31**, 1003 (1937)

3:9202 2,5-DICHLOROPENTENE-2 $C_5H_8Cl_2$ Beil. S.N. 11



B.P. 40–41° at 8 mm. (1) $D_4^{14.5}$ = **1.1182** (1) $n_C^{14.5}$ = **1.4683** (1)

[For prepn. of $\bar{C}$ (92% yield (1)) from cyclopropyl methyl ketone [Beil. VII-7, VII$_1$-(5)] with PCl_5 below 20° see (1); for formn. of $\bar{C}$ from 5-chloropentanone-2 (see below) with excess 50% KOH see (1).]

$\bar{C}$ with conc. H_2SO_4 gives (43% yield (1)) 5-chloropentanone-2 (3:9267).

$\bar{C}$ cannot be hydrolyzed with aq. + $CaCO_3$ but on protracted reflux (210 hrs.) with excess KOAc in abs. alc. gives 2-chloro-5-acetoxypentene-2, b.p. 81.5° at 13 mm., D_4^{15} = 1.0800, n_C^{15} = 1.4499 (1).

$\bar{C}$ on oxidn. with 3% $KMnO_4$ gives (1) acetic acid (1:1010) and acrylic acid (1:1020).

$\bar{C}$ on ozonolysis yields (1) β-chloropropionic acid (3:0460).

3:9202 (1) D'yakonov, *J. Gen. Chem. (U.S.S.R.)* **10**, 414–412 (1940); *C.A.* **34**, 7861 (1940).

With alc. NaOEt. [$\bar{C}$ with EtOH/NaOEt yields (23) $CHCl_3$ (3:5050) + ethyl formate (1:3000).]

With alc. KCN. [$\bar{C}$ with EtOH/KCN gives within 1 min. (88% yield (24)) ethyl dichloroacetate (3:5850): cf. behavior of chloral (3:5210) with KCN in various alcohols.]

With acid chlorides. [$\bar{C}$ with AcCl (3:7065) gives (25) the corresp. acetate [Beil. I-153], b.p. 198°. — $\bar{C}$ with isovaleryl chloride (3:7560) gives (41% yield (26)) the corresp. isovalerate, b.p. 143° at 20 mm. (26).]

With diazomethane. [$\bar{C}$ with CH_2N_2 in EtOH soln. at 0° gives (27) trichloroacetaldehyde ethyl-methyl-acetal [Beil. I-621, I_2-(681)], b.p. 193.4° cor. (28), 78–80° at 13 mm. (27) accompanied by 3,3,3-trichloro-1,2-epoxypropane (3:5760).]

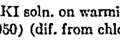
- Ⓟ Behavior on heating. Note that $\bar{C}$ on htg. gives off inflammable vapor (EtOH) (dif. from chloral hydrate (3:1270) whose initial ignition cannot be maintained).
- Ⓟ Behavior with conc. HNO_3. $\bar{C}$ reacts violently on warming with conc. HNO_3 (dif.) from chloral hydrate (3:1270) which is almost unaffected).
- Ⓟ Iodoform test. $\bar{C}$ with aq. alk. + I_2/KI soln. on warming gives iodoform, m.p. 119° accompanied of course by $CHCl_3$ (3:5050) (dif. from chloral hydrate (3:1270)).

3:0860 (1) Jacobsen, *Ann.* **157**, 244–245 (1871). (2) Willcox, Brunel, *J. Am. Chem. Soc.* **38**, 1821–1841 (1916). (3) Kuntze, *Arch. Pharm.* **246**, 98 (1908). (4) Post, *J. Org. Chem.* **6**, 830–835 (1941). (5) Leopold, *Z. physik. Chem.* **66**, 359–380 (1909). (6) Trillat, *Bull. soc. chim.* (3) **17**, 233–234 (1897). (7) Lieben, *Ber.* **3**, 909–910 (1870). (8) Nagai, *Biochem. Z.* **152**, 268 (1924). (9) Martius, Mendelssohn-Bartholdy, *Ber.* **3**, 444 (1870). (10) Kurnakow, Efrema, *Z. physik. Chem.* **85**, 411–418 (1913).

(11) Magnani, McElvain, *J. Am. Chem. Soc.* **60**, 2212 (1938). (12) Personne, *Compt. rend.* **69**, 1363 (1869). (13) Grabowsky, Herold, *Z. physik. Chem.* **B-28**, 290–302 (1935). (14) Buthmann, *Z. physik. Chem.* **B-23**, 100–104 (1933). (15) Chattaway, Backeberg, *J. Chem. Soc.* **125**, 1097–1101 (1924). (16) Bruner, *Cent.* **1902**, I 978. (17) Beckmann, *Z. physik. Chem.* **2**, 724–728 (1888). (18) Willcox, Brunel, *J. Am. Chem. Soc.* **38**, 2533–2535 (1916). (19) Byasson, *Bull. soc. chim.* (2) **32**, 304 (1879); *Compt. rend.* **87**, 26 (1878). (20) Neher, Foster, *J. Am. Chem. Soc.* **31**, 410–412 (1909).

(21) Paterno, Pisati, *Gazz. chim. ital.* **2**, 333–338 (1872). (22) Henry, *Ber.* **4**, 101, 435–438 (1871). (23) Kekulé, *Ann.* **119**, 188–189 (1861). (24) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1042. (25) Meyer, Dulk, *Ann.* **171**, 69–72 (1874). (26) Fourneau, Florence, *Bull. soc. chim.* (4) **47**, 353 (1930). (27) Meerwein, Bersin, Burneleit, *Ber.* **62**, 1002, 1007–1009 (1929). (28) Magnanni, *Gazz. chim. ital.* **16**, 331 (1886). (29) Adams, *J. Pharmacol.* **78**, 340–345 (1943); *C.A.* **37**, 6035 (1943).

3:0870 1,2,3,4-TETRACHLOROBUTADIENE-1,3 $C_4H_2Cl_4$ Beil. S.N. 12
(Solid stereoisomer)



M.P. 50° (1)

[*See also the liquid stereoisomer* (3:6150).]

[For isolation of $\bar{C}$ from the high-boilg. fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1).]

$\bar{C}$ adds Cl_2 (although much more slowly than its liquid stereoisomer) yielding 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80° (1). [This product with Zn/Cu couple in hot alc. regenerates $\bar{C}$, but in alc. with $Ca(OH)_2$ or with alk. at room temp. gives the liquid stereoisomer (3:9046) (1).]

$\bar{C}$ in $CHCl_3$ treated with Br_2 gives (100% yield (1)) 1,2-dibromo-1,2,3,4-tetrachlorobutene-2, m.p. 105° (1). [This prod. with Zn/Cu couple in hot alc. regenerates $\bar{C}$ (1).]

3:0870 (1) Müller, Hüther, *Ber.* **64**, 589–600 (1931); *C.A.* **25**, 3956 (1931).

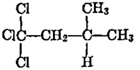
oxalic acid see (1); for formn. of C̄ (together with other products) from 2-methylbutene-1 (1:8210) by actn. of Cl_2 see (2).]

[For behavior of C̄ with NaI in acetone see (2); for use in prepn. of unsatd. cellulose ethers see (3).]

C̄ with O_3 followed by hydrolysis yields (2) chloromethyl ethyl ketone (3:8012).

3:9214 (1) Chalmers, *Trans. Roy. Soc. Can.* (3) **22**, III 73, 76 (1928). (2) Gutner, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1062–1067 (1938), *Cent.* **1939**, II 4221; *C.A.* **33**, 3755 (1939). (3) Hahn (to du Pont), U.S. 2,082,797, June 8, 1937; *Cent.* **1937**, II 3838; *C.A.* **31**, 5577 (1937).

3:9216 4,4,4-TRICHLORO-2-METHYLBUTANE $C_5H_9Cl_3$ **Beil. I-136**
("Isobutylchloroform") I_1— I_2—



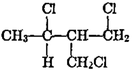
No physical constants of C̄ have been reported.

[For formn. of C̄ from diisoamyl sulfide [Beil. I-405, I_1-(200), I_2-(435)] by action of Cl_2 see (1).]

C̄ on htg. in a s.t. for 5 hrs. at 110° with Ag_2O + aq. yields (1) isovaleric acid (1:1050).

3:9216 (1) Spring, Lecrenier, *Bull. soc. chim.* (2) **48**, 627 (1887).

3:9218 *d,l*-1,3-DICHLORO-2-(CHLOROMETHYL)BUTANE $C_5H_9Cl_3$ **Beil. S.N. 10**



B.P. 79–81° at 15 mm. (1) D_4^{15} = **1.2793** (1) n_α^{15} = **1.4899** (1)
n_β^{15} = **1.4970** (1)

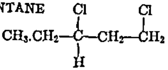
[For formn. of C̄ from 1,3-dichloro-2-methylbutane (3:9228) or from 3-chloro-2-methylbutene-1 (3:7300) with Cl_2 see (1).]

C̄ with Cl_2 as specified (1) yields 1,2,3-trichloro-(2-chloromethyl)butane (3:5230).

C̄ with KOH or with quinoline gives (1) only resins.

3:9218 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936); *Cent.* **1937**, I 573; *C.A.* **31**, 1003 (1937).

3:9220 *d,l*-1,3-DICHLOROPENTANE $C_5H_{10}Cl_2$ **Beil. S.N. 10**



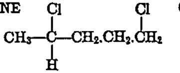
B.P. 80.4° at 60 mm. (1) D_4^{20} = **1.0834** (1) n_D^{20} = **1.4485** (1)

[For prepn. of C̄ (30% yield (1) together with other products) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1).]

C̄ on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 3-chloro-1-iodopentane, b.p. 50.5° at 2.5 mm., D_4^{20} = 1.6611, n_D^{20} = 1.5229 (1). (A small amt. of 1,3-diiodopentane, b.p. 80–82° at 2.5 mm., is also formed (1).) [For reactn. of 3-chloro-1-iodopentane with diethylamine to give (74% yield) 3-chloropentyl-diethylamine HCl, m.p. 98.5°, see (1).]

3:9220 (1) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941).

3:9224 d,l-1,4-DICHLOROPENTANE $C_5H_{10}Cl_2$ Beil. I-131
I_1—
I_2—



B.P. 88.1° at 60 mm. (1) $D_4^{20} = 1.0840$ (1) $n_D^{20} = 1.4503$ (1)
69–70° at 28 mm. (3)
59–61° at 17 mm. (2)
58–60° at 15 mm. (2)

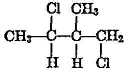
[For prepn. of C̄ (31% yield (1) together with other prods.) from 1-chloropentane (3:7460) by vapor-phase photochemical chlorination see (1); from 2-methyltetrahydrofuran [Beil. XVII-12] on htg. in s.t. for 4 hrs. at 60° with 2 vols. conc. HCl (2) or from pentanediol-1,4 by treatment in boilg. aq. with HCl (2) see indic. refs. — For formn. of C̄ (together with other prods.) from pentane (1:8505) + Cl_2 see (3).]

C̄ on boilg. with aq. (2) or aq. K_2CO_3 (3) yields pentanediol-1,4 [Beil. I-480] [*bis-(N-phenylcarbamate)*, m.p. 125–125.5° (3)].

C̄ on refluxing 24 hrs. with NaI in acetone gives (90% yield (1)) 4-chloro-1-iodopentane, b.p. 61.3° at 3.5 mm., $D_-^{20} = 1.6580$, $n_D^{20} = 1.5248$ (1) (a small amt. of 1,4-diiodopentane, b.p. 100° at 5 mm. is also formed (1)). [For reactn. of 4-chloro-iodopentane with diethylamine to give (42% yield) 4-chloropentyl-diethylamine hydrochloride, m.p. 99°, see (1).]

3:9224 (1) Hass, Huffman, *J. Am. Chem. Soc.* **63**, 1233–1235 (1941). (2) Fröbe, Hochstetter, *Monatsh.* **23**, 1087–1088 (1902). (3) Lemke, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1995–1998 (1937); *Cent.* **1939**, I 2398; *C.A.* **32**, 482 (1938).

3:9228 d,l-1,3-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. S.N. 10

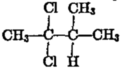


Note that C̄ has never been reported; the prod. originally supposed by (1) to have been C̄ was later (2) found to be 2-(chloromethyl)-3-chlorobutene-1 (3:9206) q.v.

By chlorination of opt. act. 1-chloro-2-methylbutane with SO_2Cl_2 in pres. of benzoyl peroxide followed by subsequent fractionation (3) both opt. act. forms of C̄ are alleged to have been obtd.; *dextro* form, b.p. 155° at 760 mm. (calcd.), 91° at 100 mm. (obs.); *levo* form, b.p. 153° at 760 mm. (calcd.), 89.2° at 100 mm. (obs.) (3). Note, however, that in (3) the authors were apparently unaware of the correction mentioned above.

3:9228 (1) Tishche [illegible] *C.A.* **31**, 1003 (1937). ([illegible] (3) Brown, Kharasch, [illegible]

3:9230 d,l-3,3-DICHLORO-2-METHYLBUTANE $C_5H_{10}Cl_2$ Beil. I-135
I_1—
I_2—



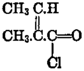
No data on physical properties of C̄ appear to be recorded.

[For prepn. of C̄ from isopropyl methyl ketone (1:5410) with PCl_5 see (1).]

C̄ with alc. KOH at 130° yields (1) isopropylacetylene (1:8010), b.p. 28°.

3:9230 (1) Béhal, *Ann. chim.* (6) **15**, 285–286 (1888).

3:9240 TIGLYL CHLORIDE (*cis*-α-Methylcrotonoyl chloride; *cis*-α,β-dimethylacryloyl choride)



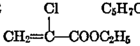
C_5H_7OCl Beil. II-431; II_1—; II_2—

B.P. 64° at 35 mm. (1)
45° at 12 mm. (2)

[For prepn. of C̄ from tiglic acid (1:0420) with PCl_3 (yield 90% (1)) (2) see indic. refs.]
C̄ with hydrazine hydrate (2 moles) yields (3) *N*,*N'*-ditiglylhydrazide, m.p. 182–183° (3).
C̄ on hydrolysis yields tiglic acid (1.0420), m.p. 64.5–65°, q.v. for the corresp. amide, anilide, *p*-toluidide, and other derivs.

3:9240 (1) Barger, Martin, Mitchell, *J. Chem. Soc.* **1937**, 1822. (2) Blaise, Bagard, *Ann. chim.* (8) **11**, 120 (1907). (3) Freri, *Atti X° congr. intern. chim.* **3**, 150–154 (1939); *Cent.* **1939**, II 3975; *C.A.* **34**, 100 (1940).

3:9242 ETHYL α-CHLOROACRYLATE



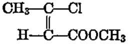
$C_5H_7O_2Cl$ Beil. S.N. 163

B.P. 51–53° at 18 mm. (1) n_D^{20} = **1.4384 (1)**

[For prepn. of C̄ from ethyl α,β-dichloropropionate (3.6090) by htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under N_2 (81% yield) see (1).]
See also α-chloroacrylic acid (3.1445) and methyl α-chloroacrylate (3·9096).

3:9242 (1) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940).

3:9244 METHYL β-CHLOROCROTONATE $C_5H_7O_2Cl$ Beil. II —; II_1-(189); II_2-(396)



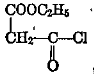
B.P. 64–67° at 14 mm. (1)
$D_4^{22.3}$ = **1.1555 (1)**
$D_4^{21.4}$ = **1.1564 (1)** $n_D^{21.4}$ = **1.46275 (1)**
D_4^{20} = **1.157 (1)**

[*See also methyl β-chloroisocrotonate* (3:8028).]

[For prepn. of C̄ from β-chlorocrotonic acid (3·2625) in MeOH (1.6120) with dry HCl see (1).]
[C̄ with Na salt of benzyl mercaptan gives (2) methyl β-(benzylmercapto)crotonate, cryst. from ether and MeOH, m.p. 69–70° (2), 73° (3), also obtd. (78% yield (3)) from Na thioenolate of methyl β-mercaptocrotonate with benzyl chloride (3.8535); note that this (and also other, analogous products) are also obtd. starting with the stereoisomeric methyl β-chloroisocrotonate (3:8028) q.v.]

3:9244 (1) von Auwers, *Ber.* **45**, 2806–2807 (1912). (2) Scheibler, Voss, *Ber.* **53**, 384 (1920). (3) Scheibler, Topouzada, Schulze, *J. prakt. Chem.* (2) **124**, 20 (1940).

3:9246 ETHYL (CHLOROFORMYL)ACETATE $C_5H_7O_3Cl$ Beil. II - 582
(Carbethoxyacetyl chloride) II_1-(252)
II_2-(529)



B.P. 75–77° at 17 mm. (1)
71° at 15 mm. (2)
68–70° at 13 mm. (3)
63–64° at 10 mm. (4)

[*See also methyl (chloroformyl)acetate* (3:9098-*A*).]

Note that C̄ is both an acid chloride and an ester; it comprises the half acid chloride/half ethyl ester of malonic acid (1:0480).

[For prepn. of C̄ from ethyl hydrogen malonate with $SOCl_2$ (3) or better from potassium ethyl malonate with $SOCl_2$ at 0° (1) or in ether (4) (yields: 70% (1), 45% (4)) cf. (5) or with PCl_5 (6) see indic. refs.]

C̄ boils at ord. press. about 170–180° with serious decompn. (3). — C̄ on repeated distn. even under reduced press. (4) or C̄ with quinoline in dry ether at 0° (4) loses HCl and undergoes condensation yielding ethyl 6-ethoxy-2,4-diketo-2,3-dihydropyran-3-carboxylate [Beil. $XVIII_1$-(540)], cryst. from CS_2, m.p. 85–86° (4) cf. (7).

[For behavior of C̄ with 2,4-dimethylpyrryl MgBr (8), with indolyl MgBr (5), with indolyl MgI (9), or with imidazolyl MgBr (10) see indic. refs.]

[For behavior of C̄ with atoxyl see (1).]

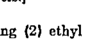
[C̄ with urea (2 moles) reacts as an acid chloride giving (2) ethyl malonurate [Beil. III-66], m.p. 128° (2). — C̄ with thioformamide condenses with loss of H_2O + HCl giving (11) (12) (13) ethyl thiazole-5-carboxylate, b.p. 103.5–104.5° at 12 mm. (13), which on hydrolysis gives thiazole-5-carboxylic acid, m.p. 196–197° cor. (11).]

—— ω-(Carbethoxyacet)anilide: unreported.
Ⓓ ω-(Carbethoxyacet)-*p*-toluidide: m.p. 83° (4).

3:9246 (1) Morgan, Walton, *J. Chem. Soc.* **1931**, 1744–1745. (2) Boehringer und Söhne, Ger. 193,447, Dec. 28, 1907; *Cent.* **1908**, I 1000; *C.A.* **2**, 1862–1863 (1908). (3) Marguery, *Bull. soc. chim.* (3) **33**, 546–547 (1905). (4) Staudinger, Becker, *Ber.* **50**, 1023 (1917). (5) Oddo, Albanese, *Gazz. chim. ital.* **57**, 833–834 (1927). (6) van't Hoff, *Ber.* **7**, 1572 (1874). (7) Leuchs, *Ber.* **39**, 2642-2643 (1906). (8) Ingraffia, *Gazz. chim. ital.* **64**, 780–782 (1934). (9) Majima, Shigematsu, Rokkaku, *Ber.* **57**, 1454–1455 (1924). (10) Oddo, Quintino, *Gazz. chim. ital.* **58**, 595–596 (1928).

(11) Erlenmeyer, von Meyenburg, *Helv. Chim. Acta* **20**, 205 (1937). (12) Soc. Chem. Ind. Basel, Swiss 192,849, Nov. 16, 1937; *Cent* **1938**, I 3659; *C.A.* **32**, 4285 (1938). (13) Soc. Chem. Ind. Basel, Ger. 658,353, March 29, 1938, *Cent.* **1938**, II 354; *C.A.* **32**, 4727 (1938).

3:9247 METHYL β-(CHLOROFORMYL)PROPIONATE Beil. S.N. 172
((β-Carbomethoxy)propionyl chloride)



B.P. 93° at 18 mm. (1) (2)
92–93° at 18 mm. (3)
89–90° at 15 mm. (3)
85–87° at 15 mm. (4)
85.5–87° at 13 mm. (3)
84° at 12 mm. (5)

Note that C̄ is both an acid chloride and an ester; C̄ is an important reagent for introducing the three-carbon radical —CH_2 CH_2.COOH.

[For prepn. of C̄ from methyl hydrogen succinate, m.p. 58° (itself obtd. (yields: 95–96% (3), 83% (4) (1)) from succinic anhydride (1:0710) with MeOH (1:6120)) by action of $SOCl_2$ (yields: 100% (6), 90–93% (3), 90% (5)) or of PCl_5 (92.5% yield (4)) see indic. refs. Note that C̄ on distn. (except at low press.) tends to lose MeCl (3:7005) giving (3). succinic anhydride (1:0710).

Examples of utility of C̄ in synthesis include the following: C̄ + ethyl sodio-acetoacetate (6); C̄ + ethyl sodio-α-acetyl-*n*-undecanoate (7); C̄ + ethyl sodio-α-acetyl-γ-phenoxy-*n*-butyrate (8); C̄ + ethyl sodio-γ-phenoxypropylacetoacetate (9); C̄ + methyl γ-(6-methoxy-1-naphthyl)butyrate (10); C̄ + methyl sodio-α-acetylpropionate (11); C̄ + 1-methylcyclohexene-1 (5); C̄ + ethyl α-acetyl-*n*-tridecanoate (1); C̄ + Cd diisoamyl (4).]

—— β-(Carbomethoxy)propionamide: unreported.

Ⓓ β-(Carbomethoxy)propionanilide: ndls. from ether or lt. pet./C_6H_6, m.p. 97–99° (1). [From C̄ with aniline (1).]

3:9247 (1) G. M. Robinson, R. Robinson, *J. Chem. Soc* **127,** 180 (1925). (2) Clutterbeck, R Robinson, *Biochem. J.*, **19,** 385–396 (1925); *Cent.* **1925,** II 1516 (3) Cason, *Org. Syntheses* **25,** 19–22 (1945) (4) Cason, *J. Am Chem Soc.* **64,** 1107 (1942) (5) Nenitzescu, Cioranescu, Przemetzky, *Ber* **73,** 314 (1940). (6) Ruggli, Maeder, *Helv. Chim. Acta* **25,** 943 (1942); *C A.* **37,** 1714–1715 (1943). (7) G. Robinson, R Robinson, *J. Chem. Soc* **1926,** 2206. (8) R. Robinson, Watt, *J. Chem Soc.* **1934,** 1539. (9) Barger, R. Robinson, Smith, *J. Chem. Soc.* **1937,** 724. (10) R. Robinson, Thompson, *J. Chem Soc.* **1938,** 2011.
(11) R. Robinson, Seijo, *J. Chem. Soc.* **1941,** 585.

3:9250 β-METHOXYETHYL TRICHLOROACETATE $C_5H_7O_3Cl_3$ Beil. S.N. 160

(Methyl " cellosolve " trichloroacetate)

CH_2OCH_3
|
$CH_2OCOCCl_3$

B.P.			M.P.		
98.0–99.5°	at 17 mm.	(2)	14.6–14.8° (1)	D_4^{20} = 1.3866 (3)	n_D^{20} = 1.45626 (2)
92–93°	at 10 mm.	(1)		1.3826 (2)	1.45823 (2)
61°	at 0.9 mm.	(3)			

Colorless liq. with agreeable odor.

[For prepn. (82% yield (1)) from β-methoxyethanol (1:6405) + trichloroacetyl chloride (3:5420) see (1).]

C̄ on shaking with ac. is smoothly saponified (1) to β-methoxyethanol (1:6405) + trichloroacetic ac. (3:1150).

3:9250 (1) Meerwein, Sönke, *Ber.* **64,** 2379 (1931). (2) Palomaa, Salmi, Korte, *Ber.* **72,** 797 (1939). (3) Meerwein, Sönke, *J. prakt. Chem* (2) **137,** 309 (1933).

3:9260 *d,l*-γ-CHLORO-*n*-VALERYL CHLORIDE $C_5H_8OCl_2$ Beil. II — II_1-(132) II_2—

$CH_3.CH(Cl).CH_2\,CH_2—C(Cl)=O$

B.P. 61° at 8 mm. (1)

[For prepn. of C̄ from γ-chloro-*n*-valeric acid (3:9270) with sl. excess of $SOCl_2$ (100% yield) see (1).]

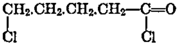
[C̄ with EtZnI at −15° to −20° yields (2) γ-chloro-*n*-butyl ethyl ketone (6-chlorohepta-

none-3) [Beil. I_1-(359)], b.p. 79° at 13 mm. (2) (semicarbazone, m.p. 129–129.5° (2), p-nitrophenylhydrazone, unrecryst. oil (2)); C̄ with C_6H_5ZnBr at 0° yields (3) γ-chloro-n-butyl phenyl ketone [Beil. VII_1-(173)], b.p. 155–156° at 15 mm. (3) (semicarbazone, m p. 123° (3)).]

C̄ on hydrolysis with aq. yields (1) γ-chloro-n-valeric acid (3:9270); for the amide, anilide, and other derivs. corresp. to C̄ see the acid (3:9270).

3:9260 (1) Wohlgemuth, *Compt. rend.* **159**, 80 (1914); *Ann. chim.* (9) **2**, 301 (1914). (2) Wohlgemuth, *Ann. chim.* (9) **2**, 405–406, 410–412 (1914). (3) Ref. 2, 417–419.

3:9264 δ-CHLORO-n-VALERYL CHLORIDE $C_5H_8OCl_2$ **Beil. S.N. 162**

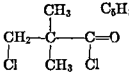


B.P. 75–80° at 5–8 mm. (1)

[For prepn. of C̄ from δ-chloro-n-valeric acid (3:0075) with $SOCl_2$ see (1).]

3:9264 (1) Child, Pyman, *J. Chem. Soc.* **1931**, 41.

3:9266 CHLOROPIVALYL CHLORIDE $C_5H_8OCl_2$ **Beil. S.N. 162**
(β-Chloro-α,α-dimethylpropionyl chloride)



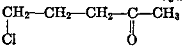
B.P. 85–86° at 60 mm. (1) n_D^{20} = **1.4539 (1)**

[For prepn. of C̄ from pivalyl chloride (trimethylacetyl chloride) (3:7450) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 see (1).]

Ⓓ **Chloropivalamide:** pl. from aq., m.p. 108–109° (1).

3:9266 (1) Kharasch, Brown, *J. Am. Chem Soc.* **62**, 925–929 (1940)

3:9267 5-CHLOROPENTANONE-2 C_5H_9OCl **Beil. I —**
(γ-Chloro-n-propyl methyl ketone) I_1—
I_2-(738)



B.P. 76° at 34 mm. (6) D_4^{18} = **1.0571 (1)** n_F^{18} = **1.4461 (1)**
74–75° at 23 mm. (1) n_C^{18} = **1.4371 (1)**
71–72° at 20 mm. (2)

[For prepn. of C̄ from 2,5-dichloropentene-2 (3:9202) by hydration with conc. H_2SO_4 (43% yield) see (1); from 2,5-epoxypentene-1 ("α-methylenetetrahydrofuran") (for whose prepn. + characteristics see (3)) by ring cleavage with conc. HCl see (4); from cyclopropyl methyl ketone cyanohydrin ("acetyltrimethylene cyanohydrin") with conc. HCl by ring cleavage and loss of HCN see (5); from α-acetobutyrolactone with HCl as directed see (6).]

[C̄ with 50% excess KOH on refluxing loses HCl and ring-closes giving (60% yield (2)) (5) *cyclopropyl methyl ketone [Beil. VII-7, VII_1-(7)], b.p. 112–113° (5),* D_4^{20} = 0.8993, n_D^{20} = 1.4244 (corresp. semicarbazone, m.p. 120–121° (5)).]

Ⓓ **5-Chloropentanone semicarbazone:** m.p. 92–93° (5), 91–92° (1).

3:9267 (1) D'yakonov, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 414–426 (1940); *C.A.* **34**, 7861 (1940). (2) Zelinsky, Dengin, *Ber.* **55**, 3360 (1922). (3) Paul, *Bull. soc. chim.* (4) **53**, 425–426 (1933); (5) **2**, 752–754 (1935). (4) Topchiev, Russ. 57,345, June 30, 1940; *C.A.* **36**, 2509 (1942). (5) [illegible]

3:9268 1-CHLOROPENTANONE-3 C_5H_9OCl Beil. I-680

(β-Chloroethyl ethyl ketone) $CH_3.CH_2—\underset{\underset{O}{\|}}{C}—CH_2.\underset{\underset{Cl}{|}}{CH_2}$ I_1— I_2—

B.P. 68° at 20 mm. (1)
48–50° at 13 mm. (2)
57° at 9 mm. (1)

[For prepn. of C̄ from propionyl chloride (3:7170) with ethylene + $AlCl_3$ with or without diluent (50% yield (4)) (2), or over suitable cat. at 100–300° and at 20–200 atm. press. (3), see indic. refs.; from β-chloropropionyl chloride (3:5690) with $ZnEt_2$ in toluene (70% yield) see (1).]

C̄ with hot aq. alk. or alk. carbonates gives only resins, but C̄ on boilg. with dry diethylaniline loses HCl yielding (1) ethyl vinyl ketone [Beil. I-731, I_2-(791)], b.p. 96°.

[C̄ with diethyl sodio-malonate in ether gives (5) diethyl α-(γ-keto-*n*-amyl)malonate, b.p. 166° at 14 mm. (5); C̄ with sodio-acetylacetone yields (5) the triketone 3-acetyloctanedione-2,6, b.p. 154° at 16 mm. (5); C̄ with ethyl sodio-acetoacetate in ether yields (6) the expected ethyl octandione-2,6-carboxylate-3 (3-carbethoxyoctanedione-2,6), b.p. 150° at 8 mm. (6).]

[C̄ with diethylamine in ether in cold, followed by treatment with dil. aq. alk., yields (7) 1-diethylaminopentanone-3, b.p. 84° at 13 mm., n_D^{15} = 1.4368 (7).]

[C̄ with aniline (2 moles) + a little water reacts vigorously on warming yielding (8) 1-anilinopentanone-3 [Beil. XII-214], tbls. from ether, m.p. 55.5° (8); note, however, that C̄ with aniline htd. in abs. alc. or C_6H_6 (8), or C̄ with aniline htd. with conc. HCl (or 40% H_2SO_4) + nitrobenzene (or H_3AsO_4), gives (9) (4) 4-ethylquinoline [Beil. XX-406, XX_1-(153)].]

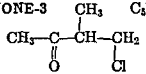
[C̄ with hydrazine hydrate in MeOH gives (80% yield (10)) by ring closure 3-ethyl-Δ^2-pyrazoline [Beil. XXIII-32], liq., b.p. 76° at 22 mm. (10) (corresp. picrate, B.PkOH, yel. ndls. from 95° alc., m.p. 117° (10)). — C̄ with phenylhydrazine in ether gives (10) by ring closure 3-ethyl-1-phenyl-Δ^2-pyrazoline [Beil. XXIII-32], oil, b.p. 155° at 9 mm. (10).]

[C̄ with $NH_2OH.HCl$ + K_2CO_3 in aq. MeOH htd. for a few minutes gives (20% yield (10)) by ring closure 3-ethyl-Δ^2-isoxazoline [Beil. XXVII-13], oil, b.p. 69° at 11 mm. (10).]

Ⓓ **1-Carbamido-3-ethyl-Δ^2-pyrazoline:** cryst. from EtOAc or C_6H_6, m.p. 96° (10). [Note that C̄ with 1 equiv. semicarbazide HCl + NaOAc in aq. immediately ppts. the corresp. semicarbazone; this on htg. with strong aq. NaOAc (or C̄ + semicarbazide HCl + strong NaOAc soln. htd. directly) loses HCl and ring-closes to the indic. deriv. (10).]

3:9268 (1) Blaise, Maire, *Bull. soc. chim.* (4) **3**, 268–271 (1908); *Compt. rend.* **142**, 216 (1906). [illegible] 26, 1929; *Cent.* **1930**, II 1133; Brit. 282,412, [illegible] zevich (to Standard Oil Development Co.), [illegible] (4) Kenner, Statham, *Ber.* **69**, 16–17 (1936). [illegible] 908) (6) Blaise, Maire, *Bull. soc. chim.* (4) [illegible] inson, Simonsen, *J. Chem. Soc.* **1937**, 1578. [illegible] –665 (1908) (9) Schering-Kahlbaum, A.G., [illegible] (10) Blaise, Maire, *Bull. soc. chim.* (4) **3**, 272–279 (1908).

3:9269 1-CHLORO-2-METHYLBUTANONE-3 C_5H_9OCl Beil. S.N. 87

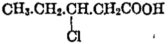


B.P. 60–62° at 16 mm. (1)

[For prepn. of C̄ from 2-methylbutanon-3-ol-1 (β-acetyl-*n*-propyl alc.) [Beil. I_1-(422)] with 3 moles HCl (satd. at 0°), *preferably in pres. of 5–10%* $AlCl_3$ (*50% yield*, accompanied by some 2-methylbuten-1-one-3, b.p. 96–99°) see (1).]

3:9269 (1) Decombe, *Compt. rend.* **202**, 1685–1687 (1936); *Cent.* **1936**, II 1525.

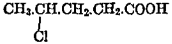
— *d,l*-β-CHLORO-*n*-VALERIC ACID $C_5H_9O_2Cl$ Beil. S.N. 162



B.P. 112° at 10 mm. **M.P. 33°** D_4^{20} **= 1.1484** n_D^{20} **= 1.4462**

See 3:0270. *Division A: Solids.*

3:9270 *d,l*-γ-CHLORO-*n*-VALERIC ACID $C_5H_9O_2Cl$ Beil. II — II_1-(131) II_2—



B.P. 117° at 10 mm. (1) D_4^{20} **= 1.1514 (1)** n_D^{20} **= 1.4458 (1)**
115–116° at 10 mm. (2) **1.1510 (1)** **1.4456 (1)**

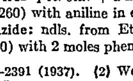
[*For prepn. of* C̄ *from* γ-*n*-*valerolactone* (*1:5080*) *with conc.* HCl *at 150°* see (2); from β-ethylidene-propionic acid (penten-3-oic acid-1) [Beil. II-426, II_1-(191), II_2-(400)] or from allyl-acetic acid (penten-4-oic acid-1) [Beil. II-425, II_1-(191), II_2-(399)] with dry HCl gas in ether or heptane at −15° see (1).] [For opt. act. isomers of C̄ see Beil. II_2-(268) and subsequent literature.]

C̄ with $SOCl_2$ yields (2) γ-chloro-*n*-valeryl chloride (3:9260).

— Methyl γ-chloro-*n*-valerate: unrecorded.
— Ethyl γ-chloro-*n*-valerate: b.p. 196° (see 3:8703).
Ⓓ γ-Chloro-*n*-valeramide: tbls. from ether, m.p. 79–79.5° (2). [From γ-chloro-*n*-valeryl chloride (3:9260) with conc. aq. NH_4OH (2).]
Ⓓ γ-Chloro-*n*-valer-anilide: ndls. from pet. eth. + a little AcOH, m.p. 104° (2). [From γ-chloro-*n*-valeryl chloride (3:9260) with aniline in ether soln. (2).]
Ⓓ γ-Chloro-*n*-valero-phenylhydrazide: ndls. from EtOAc, m.p. 100° (2). [From γ-chloro-*n*-valeryl chloride (3:9260) with 2 moles phenylhydrazine in ether (2).]

3:9270 (1) Schjanberg, *Ber.* **70**, 2385–2391 (1937). (2) Wohlgemuth, *Compt. rend.* **158**, 1577 (1914); *Ann. chim.* (9) **2**, 298–304 (1914).

— CHLOROPIVALIC ACID $C_5H_9O_2Cl$ Beil. S.N. 162



B.P. 126–129° at 30 mm. **M.P. 40–42°**

See 3:0440. *Division A: Solids.*

3:9280 β-ETHOXYETHYL CHLOROFORMATE $C_5H_9O_3Cl$ **Beil. S.N. 199**
(" Cellosolve " chloroformate; $C_2H_5.O.CH_2.CH_2.O.CO.Cl$
β-ethoxyethyl chlorocarbonate)

B.P. 67.2° at 14 mm. (1) D^{25}_{abs} **= 1.1341 (1)** n^{25}_{D} **= 1.4169 (1)**

Colorless liq. insol. aq.
[For prepn. (77% yield (1)) from β-ethoxyethanol ("Cellosolve") (1:6410) + phosgene (3:5000) see (1).]

Ⓓ β-Ethoxyethyl carbamate: m.p. 62.2° (1). [From C̄ + aq NH_4OH in 39% yield; cryst. from propylene chloride (1).]

3:9280 (1) Asburn, Collett, Lazzell, *J. Am. Chem Soc.* **60**, 2933–2934 (1938).

3:9285 β-METHOXYETHYL CHLOROACETATE $C_5H_9O_3Cl$ **Beil. S.N. 160**
(Methyl " cellosolve " chloroacetate)

$CH_2.O.CH_3$
|
$CH_2.O.CO.CH_2Cl$

B.P. 85–86° at 9 mm. (1) D^{20}_{4} **= 1.2015 (1)** n^{20}_{D} **= 1.43821 (1)**
60° at 1.3 mm. (1)

Colorless oil.
[For prepn. (80% yield (1)) from ethylene glycol monomethyl ether (1:6405) + chloroacetyl chloride (3:5235) in $CHCl_3$ see (1).]
C̄ on shaking with aq. saponifies to β-methoxyethanol (1:6405) + chloroacetic ac. (3:1370); titration of aq. soln. neutralizes 1 equiv. alk. (i.e., Sap. Eq. = 188.5).

3:9285 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 319–320 (1933).

3:9287 *ter*-AMYL HYPOCHLORITE $C_5H_{11}OCl$ **Beil. I —**
(Dimethyl-ethyl-carbinyl hypochlorite) **I_1—**
I_2-(423)

CH_3
|
$CH_3.CH_2—C—CH_3$
|
OCl

B.P. see text. D^{25}_{4} **= 0.8547 (1)**

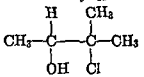
[*See also ter-butyl hypochlorite* (3:7165).]

Yellow mobile liquid with irritating odor and giving vapor which violently attacks eyes and mucous membranes (1). — C̄ boils with considerable decomposition; a thermometer in the vapor recorded 76° at 752 mm., but this cannot, of course, be regarded as a b.p. (1).
C̄ is relatively stable and even after 2 months (in dark) is practically unchanged (1); for study of stability of C̄ in aq. or in CCl_4 see (2). — C̄ on exposure to bright sunlight dec. quietly with evolution of heat leaving a colorless liq. contg acetone (1:5400) and other prods.
[For prepn. of C̄ from *ter*-amyl alc. (1:6160) with Cl_2 in aq. alk. (1) (3) or alk. earth (4) or with aq. HOCl in pres. of CCl_4 (90% yield (5)) (2) see indic. refs.]
C̄ with KI + AcOH liberates I_2 quant. according to equation $C_5H_{11}OCl + 2HI \rightarrow C_5H_{11}OH + HCl + I_2$ (use in quant. detn. of C̄ (1)).
[For reactn. of C̄ with $R_2C{=}NMgX$ cpds. to yield *N*-chloroimines see (3); for reactn. of C̄ with Schiff's bases see (5) (6).]

3:9287 (1) Chattaway, Backeburg, *J. Chem. Soc.* **123**, 2999–3003 (1923). (2) Taylor, MacMullen, Gammal, *J. Am. Chem. Soc.* **47**, 397–398 (1925). (3) Hauser, Humble, Haus, *J. Am. Chem.*

639–648 (1936); *Cent.* **1937**, I 1674; *C.A.* **31**, 3459 (1937).

3:9290 *d,l*-2-CHLORO-2-METHYLBUTANOL-3 $C_5H_{11}OCl$ Beil. I - 392
(α-Chloroisopropyl-methyl-carbinol) I_1-(196)
I_2—



No physical constants on $\bar{C}$ appear to be recorded.

[For prepn. of $\bar{C}$ from 2,3-epoxy-2-methylbutane (trimethylethylene oxide) [Beil. XVII-13] by addn. of HCl see (1).]

$\bar{C}$ passed over clay at 350° and 18 mm. pressure yields (2) 2-methylbutadiene-1,3 (isoprene) (1:8020).

3:9290 (1) Henry, *Compt. rend.* **144**, 311 (1907); *Rec. trav. chim.* **26**, 430–433 (1907). (2) Badische Anilin und Soda Fabrik, Ger. 255,519, Jan 3, 1913; *Cent.* **1913**, I 476.

3:9295 5-CHLOROPENTANOL-1 $CH_2.(CH_2)_3.CH_2OH$ (with Cl on the first CH_2) $C_5H_{11}OCl$ Beil. S.N. 24
(ω-Chloro-*n*-amyl alcohol)

B.P. 114° at 16 mm. (1)

[For prepn. of $\bar{C}$ from α,ω-pentamethylene glycol (1:6519) with $SOCl_2$ (35% yield (2)) or with S_2Cl_2 (35% yield (1)) see indic. refs.]

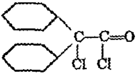
$\bar{C}$ with aliphatic mercaptans has apparently not been studied. [However, 5-chloro-*n*-amyl acetate (see below) with MeSH in MeOH/KOH yields (1) 5-hydroxy-*n*-amyl methyl sulfide, b.p. 121° at 16 mm., $D_4^{20} = 0.9846$, $n_\alpha^{20} = 1.488185$ (corresp. *N*-phenylcarbamate, m.p. 43.5°); this prod. with $SOCl_2$ gives (75% yield (3)) 5-chloro-*n*-amyl methyl sulfide, b.p. 94° at 15 mm., $D_4^{20} = 1.0300$, $n_D^{20} = 1.48597$. — Similarly 5-chloro-*n*-amyl acetate with EtSH in alc. KOH gives (68% yield (4)) 5-hydroxy-*n*-amyl ethyl sulfide, b.p. 135° at 20 mm.; this prod. with $SOCl_2$ + diethylaniline in CCl_4 gives (64% yield (4)) 5-chloro-*n*-amyl ethyl sulfide b.p. 122° at 25 mm. (4).]

$\bar{C}$ with aromatic mercaptans has apparently not been studied. [However, 5-chloro-*n*-amyl acetate (see below) with thiophenol in alc. KOH gives (1) 5-hydroxy-*n*-amyl sulfide, ndls. from lt. pet., m.p. 31.5° (corresp. *N*-phenylcarbamate, m.p. 59°); this prod. with $SOCl_2$ + dimethylaniline in $CHCl_3$ gives (3) 5-chloro-*n*-amyl phenyl sulfide, b.p. 174° at 14 mm., sl. dec., 140° at 1 mm., $D_4^{20} = 1.1065$, $n_D^{20} = 1.56040$.]

$\bar{C}$ with Et_2NH appears never to have been studied. [However, the prod. to be expected, viz., 5-(diethylamino)pentanol-1, b.p. 131° at 23–24 mm. (5), 125° at 18 mm. (6), $D_{20}^{20} = 0.8842$ (5), $n_D^{20} = 1.4642$ (5), has been reported by other means; this prod. with $SOCl_2$ in $CHCl_3$ would be expected to yield 5-(diethylamino)-*n*-amyl chloride, but this cannot be isolated in the free state owing to its isomerization (7) to *N*-ethyl 1-ethyl-2-methylpyrrolidinium chloride.]

$\bar{C}$ with morpholine gives (8) alm. quant. 5-(4-morpholinyl)pentanol-1, b.p. 133.0–133.5° at 5 mm., $D_4^{25} = 1.005$, $n_D^{24} = 1.4755$ (corresp. *N*-phenylcarbamate, m.p. 55.5–57.0° cor.) (8). — $\bar{C}$ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (2) in alm. 100% yield (as salt) *N*-(5-hydroxy-*n*-amyl)-*N'*-phenylpiperazine, m.p. 74.0–75.0° cor. (corresp. *N*-phenylcarbamate, m.p. 100.0–101.5° cor.) (2).

3:0885 α-CHLORO-DIPHENYLACETYL CHLORIDE $C_{14}H_{10}OCl_2$ Beil. IX - 675
(Diphenyl-chloro-acetyl chloride) IX_1-(283)



M.P. 51°	(1)	B.P. 180°	at 14 mm. (3)
50°	(2) (8) (11)	179-180°	at 14 mm. (8) (11)
49-50°	(3)		
48.5-49.5°	(9)		

Cryst. from lgr.

[For prepn. of Č from benzilic acid (α-hydroxy-diphenyl-acetic acid) (1:0770) with 2 moles PCl_5 at 120-130° (2), at 100° (8) (68% yield (9)), or with excess PCl_5 in C_6H_6 at room temp. (7) see indic. refs. (Note that benzilic acid dislvd in undil. $SOCl_2$ yields (4) benzophenone (1:5150), that benzilic acid treated with 3 moles $SOCl_2$ in CCl_4 for several days at room temp. ppts. (5) diphenylchloroacetic acid (3:3585), m.p. 118-119° dec., and that benzilic acid in CCl_4 with 6 moles $SOCl_2$ refluxed for several days yields (5) on concn. of the soln. diphenyl-chloro-acetic anhydride [Beil. IX_1-(228)], m.p. 129° (5).) — For formn. of Č from diphenylketene [Beil. VII-471, VII_1-(254)] with $SOCl_2$ or SO_2Cl_2 by htg. at 100° in s.t. in absence of air (1), or from diphenyldiazomethane [Beil. VII-418, VII_1-(226)] with liq. phosgene in pet. ether in s.t. (92% yield), see (6).]

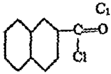
[For abnormal reactn. of Č with C_6H_5MgBr see (9) (10); for reactn. of Č with Zn filings in dry ether yielding diphenylketene (above) see (11), for reactn. of Č with phenylhydroxylamine in ether giving quant. yield of anhydro-[N-phenyl-benzilhydroxamic acid] [Beil. $XXVII_1$-(290)], cryst. from MeOH, m.p. 72-73°, see (12).]

Č in ether treated with gaseous NH_3 (2) (13) yields α-chloro-diphenylacetamide, m.p. 115° (2), 111-113° (13). [This product on boilg. with aq. yields (2) benzilamide, m.p. 154° (2).]

Č dislvd. in dry ether and treated with 2 moles aniline in dry ether ppts. aniline hydrochloride and from the filtrate addn. of pet. ether ppts. (3) α-chloro-diphenyl-acet-anilide, m.p. 88° (3); this prod. on htg. with more aniline or Č warmed with 4 moles aniline yields (3) α-anilido-diphenyl-acet-anilide, ndls. from alc., m.p. 181-182° (3). [Both the first prod. (on treatment with Na_2CO_3) and the latter prod. (on HCl hydrolysis) yield (3) benzilic acid anilide, m.p. 175° (3).]

3:0885 (1) Staudinger, Göhring, Scholler, *Ber.* **47**, 47-48 (1914). (2) Bickel, *Ber.* **22**, 1538-1539 (1889). (3) Klinger, *Ann.* **389**, 255-264 (1912). (4) Meyer, *Monatsh.* **22**, 793 (1901). (5) Stollé, *Ber.* **43**, 2471-2473 (1910). (6) Staudinger, Anthes, Pfenninger, *Ber.* **49**, 1939-1940 (1916). (7) Setlur, Nadkarni, *Proc. Indian Acad. Sci.* **12-A**, 266-269 (1940), *C.A.* **35**, 1398 (1941). (8) Staudinger, *Ann.* **356**, 72-75 (1907). (9) McKenzie, Boyle, *J. Chem. Soc.* **119**, 1137-1139 (1921). (10) Boyle, McKenzie, Mitchell, *Ber.* **70**, 2153-2160 (1937).
(11) Staudinger, *Ber.* **38**, 1735-1736 (1905). (12) Staudinger, Jelagin, *Ber.* **44**, 371-373 (1911). (13) Steinkopf, *Ber.* **41**, 3593 (1908).

3:0900 β-NAPHTHOYL CHLORIDE $C_{11}H_7OCl$ Beil. IX - 657
IX_1—



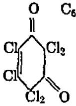
M.P. 51° (1)	B.P. 304-306° (2)	
43° (2)		

CHAPTER XXI

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9300–3:9599 (C_6–C_8 inclusive)
(Arranged in sequence of empirical formulas)

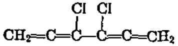
—— **1,2,4,4,6,6-HEXACHLOROCYCLOHEXEN-1-DIONE-3,5** $C_6O_2Cl_6$ Beil. VII - 272
(" Hexachlororesorcinol ") VII$_1$—



B.P. 159–160° at 13–15 mm. **M.P. 115°**

See 3:3470. *Division A: Solids.*

3:9300 3,4-DICHLOROHEXATETRAENE-1,2,4,5 $C_6H_4Cl_2$ Beil. S.N. 14

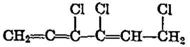


B.P. 38–40° at 8 mm. (1) D_4^{20} = **1.1819 (1)** n_D^{20} = **1.5456 (1)**

[For prepn. of Č from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10–15° (a much larger amt. of 1,3,4-trichlorohexatriene-2,4,5 (3:9302) is also formed) see (1).]

3:9300 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933).

3:9302 3,4,6-TRICHLOROHEXATRIENE-1,2,4 $C_6H_5Cl_3$ Beil. S.N. 13

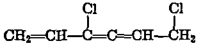


B.P. 50° at 1 mm. (1) D_4^{20} = **1.3132 (1)** n_D^{20} = **1.5517 (1)**

[For prepn. of Č from 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with 15% excess KOH in abs. MeOH at 10–15° (a small amt. of 3,4-dichlorohexatetraene-1,2,4,5 (3:9300) is also formed) see (1).]

3:9302 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933).

3:9304 3,6-DICHLOROHEXATRIENE-1,3,4 $C_6H_6Cl_2$ Beil. S.N. 13



B.P. 45–46° at 3 mm. (1) D_4^{20} = **1.1807 (1)** n_D^{20} = **1.5195 (1)**
38° at 1 mm. (1)

—— 5-Chloro-*n*-amyl acetate: b.p. 103° at 18 mm., $D_4^{20} = 1.0648$, $n_\alpha^{20} = 1.43791$ (1).
Ⓓ 5-Chloro-*n*-amyl *N*-phenylcarbamate: m.p. 72° (1).

3:9295 (1) Bennett, Heathcoat, *J Chem. Soc.* **1929**, 273–274. (2) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3439–3440 (1939). (3) Bennett, Heathcoat, Mosses, *J. Chem Soc.* **1929**, 2569–2571. (4) Bennett, Turner, *J Chem. Soc.* **1938**, 814–815. (5) Magidson, Strukow, *Arch. Pharm.* **271**, 575 (1933) (6) von Braun, *Ber.* **49**, 974 (1916). (7) Clemo, Hook, *J. Chem. Soc.* **1936**, 608–609. (8) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3440–3441 (1939).

[For prepn. of C̄ from 3,6-dichlorohexatriene-1,3,4 (3:9304) with conc. HCl contg. Cu_2Cl_2 by shaking for 12 hrs. at 27° see (1).]

C̄ refluxed with stirring for 7 hrs. with aq. Na_2CO_3 gives (1) chloride ion corresp. to three halogen atoms but the org. product was not identified.

C̄ on oxidn. with alk. $KMnO_4$ for 4 hrs. at 30–40° yields (1) chloroacetic acid (3:1370).

3:9308 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933).

3:9310 1,3-DICHLOROHEXADIENE-2,4 $C_6H_8Cl_2$ Beil. S.N. 12
(Divinylacetylene dihydrochloride)

$$CH_3{-}CH{=}CH{-}\underset{}{\overset{Cl}{\overset{|}{C}}}{=}CH{-}\overset{Cl}{\overset{|}{C}}H_2$$

B.P. 80–82° at 17 mm. (1) D_4^{20} = **1.1456 (1)** n_D^{20} = **1.5271 (1)**

[For prepn. of C̄ (53% yield (1)) from divinylacetylene by shaking with 12 *N* HCl contg. Cu_2Cl_2 see (1).]

C̄ refluxed with NaOAc + AcOH yields (by reactn. of *one* chlorine atom) 1-acetoxy-3-chlorohexadiene-2,4, b.p. 84–85° at 3 mm., D_4^{20} = 1.0915, n_D^{20} = 1.4890 (1). — Similarly C̄ on htg. with MeOH/KOH yields (1) 1-methoxy-3-chlorohexadiene-2,4, n.p. 88–92° at 30 mm., D_4^{20} = 1.0239, n_D^{20} = 1.4928 (1).

C̄ on oxidn. with aq. $KMnO_4$ in K_2CO_3 soln. gives (1) chloroacetic acid (3:1370) + acetic acid (1:1010).

C̄ with naphthoquinone-1,4 (1:9040) or with maleic anhydride (1:0625) gives (1) only a small amt. of dark gummy material.

3:9310 (1) Coffman, Nieuwland, Carothers, *J. Am. Chem. Soc.* **55**, 2048–2051 (1933).

3:9312 3-CHLOROHEXADIENE-1,3 C_6H_9Cl Beil. S.N. 12

$$CH_3.CH_2{-}CH{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

B.P. 68.2–69° at 117 mm. (1) D_4^{20} = **0.9390 (1)** n_D^{20} = **1.4770 (1)**

[For prepn. of C̄ from α-ethyl-β-vinylacetylene by shaking with conc. HCl contg Cu_2Cl_2 + NH_4Cl see (1).]

[For polymerization of C̄ see (1) (2).]

C̄ on htg. with 2 pts. naphthoquinone-1,4 (1:9040) for 2 hrs. at 100° then suspended in alc. NaOH and aerated gives (1) 2-chloro-1-ethylanthraquinone, yel. ndls. from alc., m.p. 151–152° (1).

[For study of another chlorohexadiene obtd. from allyl chloride (3:7035) by actn. of $NaNH_2$ in liq. NH_3 see (3).]

3:9312 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* **55**, 1624–1627 (1933). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; *Cent.* **1934**, II 1037; *C.A.* **28**, 3270 (1934). (3) Kharasch, Nudenberg, Sternfeld, *J. Am. Chem. Soc.* **62**, 2034–2035 (1940).

3:9314 1-CHLORO-3-METHYLPENTADIENE-1,2 C_6H_9Cl Beil. S.N. 12

$$CH_3{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}C{=}\overset{Cl}{\overset{|}{C}}H$$

B.P. 68–70° at 100 mm. (1) D_4^{20} = **0.9562 (1)** n_α^{20} = **1.46967 (1)**

[For formn. of C̄ from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking

[For prepn. of C̄ from hexadien-2,5-yne-3 (divinylacetylene) (2) with Cl_2 in CCl_4 at −50° (20–25% yield together with other products) or in small yield with HOCl see (1).]

C̄ slowly polymerizes, changing in 3 months to a viscous sirup (1).

C̄ on cat. hydrogenation in EtOAc yields *n*-hexane (1:8530), b.p. 69–70° (1).

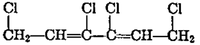
...0° gives (1) 1,3,4,6-tetrachlorohexadiene-2,4 n_D^{20} = 1.5458 (1).
12 hrs. at 27° adds HCl yielding (1) 3,3,6-trichlorohexadiene-1,4 (3:9308) q v.

C̄ refluxed with stirring for 8 hrs. with 6 pts. aq contg 2 moles Na_2CO_3 gives (1) chloride ion corresp. to one of the two initial halogenations together with a soft sticky resin. — C̄ with MeOH/KOH at 10–15° or with NaOMe in dry MeOH loses 1 HCl giving excellent yield (1) of 3-chlorohexatetraene-1,3,4,5 (3:7735).

C̄ on oxidn. with aq. $KMnO_4$ yields (1) chloroacetic acid (3.1370).

3:9304 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem. Soc.* **53**, 4200–4202 (1931).

3:9306 1,3,4,6-TETRACHLOROHEXADIENE-2,4 $C_6H_6Cl_4$ **Beil. S.N. 12**



B.P. 84–89° at 2 mm. (1) D_4^{20} **= 1.4013 (1)** n_D^{20} **= 1.5465 (1)**

[For prepn. of C̄ from hexadien-2,5-yne-3 (divinylacetylene) (2) with Cl_2 at −40° to −50° (together with other products) see (1).]

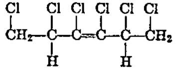
C̄ treated directly with Cl_2 for 8 hrs. at 60–70° gives (23% yield (1)) 1,2,3,4,5,6-hexachlorohexene-3 (3:1220), m p 57–58° (1)

C̄ refluxed for 8 hrs. with stirring with aq Na_2CO_3 soln. gives (1) chloride ion corresp. to two of the initial four chlorine atoms. — C̄ with abs. MeOH/KOH at 10–15° loses HCl in each of two ways yielding (1) both 1,3,4-trichlorohexatriene-2,4,5 (3:9302) and 3,4-dichlorohexatetraene-1,2,4,5 (3:9300).

C̄ on oxidn. with aq. $KMnO_4$ for 5 hrs. at 35–40° gives (1) chloroacetic acid (3:1370).

3:9306 (1) Coffman, Carothers, *J Am. Chem Soc.* **55**, 2040–2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem Soc* **53**, 4200–4202 (1931)

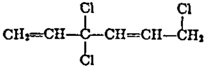
— **1,2,3,4,5,6-HEXACHLOROHEXENE-3** $C_6H_6Cl_6$ **Beil. S.N. 11**



B.P. 110–112° at 2 mm. **M.P. 58–59°**

See 3:1220. *Division A: Solids.*

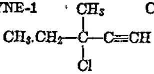
3:9308 3,3,6-TRICHLOROHEXADIENE-1,4 $C_6H_7Cl_3$ **Beil. S.N. 12**



B.P. 100–103° at 4 mm. (1) D_4^{20} **= 1.3036 (1)** n_D^{20} **= 1.5585 (1)**

3:9322 3-CHLORO-3-METHYLPENTYNE-1 C_6H_9Cl Beil. S.N. 12

(Ethyl-ethynyl-methyl-carbinyl chloride)



B.P. 55° at 130 mm. (1) D_4^{20} = 0.9163 (1) n_D^{20} = 1.4330 (1) (2)
51–52° at 135 mm. (2) 0.9140 (2)
48–50° at 100 mm. (3) 0.9141 (3) n_α^{20} = 1.42963 (3)

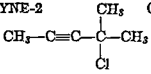
[For prepn. of C̄ from 3-methylpentyn-1-ol-3 (ethyl-ethynyl-methyl-carbinol) by shaking with *conc.* HCl (40% yield (2)) best overnight (60% yield (1)); if the acid also contains $Cu_2Cl_2 + NH_4Cl$, C̄ is accompanied (3) by 1-chloro-3-methylpentadiene-1,2 (3:9314).] [Note that dry HCl at 0° reacts with the alc. only slightly while PCl_3 + pyridine gave a product difficult to purify (1).]

C̄ with CH_3MgBr gives (66% yield (1)) 3,3-dimethylpentyne-1, b.p. 69° at 100 mm, D_4^{20} = 0.7610, n_D^{20} = 1.4360; C̄ with C_2H_5MgBr gives (61% yield (1)) 3-ethyl-3-methylpentyne-1, b.p. 88° at 100 mm., D_4^{20} = 0.7714, n_D^{20} = 1.4386. [In orig. paper these products are incorrectly numbered and named.]

... *Chem. Soc.* **62**, 1798–1800 (1940). (2) K. N. Campbell, B. K. ... **0**, 2882–2884 (1938). (3) Favorskaya, Zakharova, *J. Gen.* ... *C.A.* **34**, 7844 (1940).

3:9324 4-CHLORO-4-METHYLPENTYNE-2 C_6H_9Cl Beil. S.N. 12

(Trimethylpropargyl chloride)



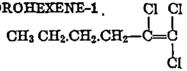
B.P. 57–61° at 47 mm. (1) n_D^{20} = 1.4143 (1)

[For prepn. of C̄ (33% yield (1)) from 2-methylpropyn-3-ol-2 (trimethylpropargyl alcohol) with PCl_3 in dry ether see (1).]

C̄ in acetone refluxed 4 hrs. with K_2CO_3 and phenol gives (69% yield (1)) phenyl trimethylpropargyl ether, n_D^{20} = 1.3408, but undistillable without decomposition (1).

3:9324 (1) Hurd, Cohen, *J. Am. Chem. Soc.* **53**, 1074 (1931).

3:9326 1,1,2-TRICHLOROHEXENE-1 $C_6H_9Cl_3$ Beil. S.N. 11



B.P. 90–93° at 10 mm. (1) (2) D_-^{25} = 1.225 (1) (2) n_D^{25} = 1.4760 (1) (2)

This compound was at first (2) thought to be 1,2,2-trichlorohexane but later (1) was established as C̄.

[For formn. of C̄ from hexyne-1 (*n*-butylacetylene) (1:8055) with Cl_2 in aq. *ter*-BuOH, MeOAc, AcOH, or Ac_2O at 45° (2) or in 35% aq. HCl, 30% aq. H_2SO_4, 30% H_3PO_4, or 22% MeOH/HCl (1) see indic. refs.]

3:9326 (1) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449–450 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460–1461 (1939).

with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1) (considerable 3-chloro-3-methylpentyne-1 (3:9322) is also formed).]

$\bar{C}$ on stdg. 8 months with Cu_2Cl_2, NH_4Cl, plus a few drops conc. HCl isomerized to 1-chloro-3-methylbutadiene-1,3 (3:7355) (1).

3:9314 (1) Favorskaya, Zakharova, *J. Gen. Chem.* (*U.S.S R.*) **10**, 446–450 (1940); *C.A.* **34**, 7844 (1940).

3:9316 1-CHLORO-3-METHYLPENTADIENE-1,3 C_6H_9Cl **Beil. S.N. 12**

$$CH_3{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}\overset{\displaystyle Cl}{\overset{|}{C}}H$$

B.P. 62–63° at 100 mm. (1) D_4^{20} = **0.9574 (1)** n_α^{20} = **1.47714 (1)**

[For prepn. of $\bar{C}$ from 1-chloro-3-methylpentadiene-1,2 (3:9314) by stdg 8 months with Cu_2Cl_2, NH_4Cl, plus a few drops conc. HCl see (1).]

$\bar{C}$ reacts with maleic anhydride (1·0625) to give a mixt. from which after hydrolysis two acids, one m.p. 218–220°, the other, m.p 350–351°, are obtd. (1).

3:9316 (1) Favorskaya, Zakharova, *J. Gen. Chem.* (*U.S.S R*), **10**, 446–450 (1940); *C.A.* **34**, 7844 (1940).

3:9318 2-CHLORO-3-METHYLPENTADIENE-1,3 C_6H_9Cl **Beil. S.N. 12**

$$CH_3{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\overset{\displaystyle Cl}{\overset{|}{C}}{=}CH_2$$

B.P. 57–60° at 96 mm. (1) D_4^{20} = **0.9437 (1)** n_D^{20} = **1.4671 (1)**

[For prepn. of $\bar{C}$ from 3-methylpenten-2-yne-4 in 22% yield (1) by shaking for 5½ hrs at 20° with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1).]

$\bar{C}$ on htg with 2 pts. naphthoquinone-1,4 (1.9040) for 1 hr. at 100° gives (1) on cooling 2-chloro-3,4-dimethyltetrahydroanthraquinone, colorless ndls *from* aq. acetone, m p 107° (1); suspension of this intermediate in dil. alc NaOH and aeration until the purple solution becomes yellow gives (1) 2-chloro-3,4-dimethylanthraquinone, yel. cryst. from AcOH, m p. 171.5° (1).

[For polymerization of $\bar{C}$ see (1) (2).]

3:9318 (1) Carothers, Coffman, *J. Am. Chem. Soc.* **54**, 4075–4076 (1932). (2) Carothers, Coffman (*to* du Pont), U.S. 1,950,441, March 13, 1934; *Cent.* **1934**, II 1038, *C.A.* **28**, 3270 (1934).

3:9320 1-CHLOROHEXYNE-1 C_6H_9Cl **Beil. S.N. 12**

$$CH_3.CH_2.CH_2\,CH_2{-}C{\equiv}C{-}Cl$$

B.P. 47° at 55 mm. (1) n_D^{-} = **1.43350 (1)**

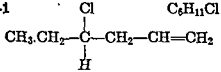
[For prepn. of $\bar{C}$ from hexyne-1 (1:8055) by conversion in liq NH_3 to $C_4H_9.C{\equiv}C{-}K$ and treatment of this prod. in ether suspension with Cl_2 at −32° see (2) (3); for prepn. of $\bar{C}$ from $C_4H_9\,C{\equiv}C.Na$ with benzenesulfonyl chloride in ether see (1) (4).]

$\bar{C}$ in MeOH + HgO + BF_3 as specified (2) adds 2 MeOH giving in 83% yield 1-chloro-2,2-dimethoxyhexane, b p 77–80° at 14 mm , D_{-}^{25} = 0 9873, n_D^{25} = 1.4305 (2).

3:9320 (1) Pflaum, Wenzke, *J. Am. Chem. Soc* **56**, 1106–1107 (1934). (2) Verbanc, Hennion, *J. Am. Chem. Soc.* **60**, 1711–1713 (1938). (3) McCusker, Vogt, *J. Am. Chem. Soc.* **59**, 1308–1309 (1937). (4) Truchet, *Ann. chim.* (10) **16**, 309–416 (1931).

3:9332 (1) Hennion, Welsh, *J. Am. Chem. Soc.* **62**, 1367–1368 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460–1461 (1939). (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449–450 (1940).

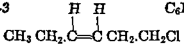
3:9334 *d,l*-3-CHLOROHEXENE-1 $C_6H_{11}Cl$ Beil. S.N. 11



[This compound is as yet unrecorded: a dextrorotatory isomeride has been prepared (1) from levorotatory hexen-1-ol-3 with PCl_3 in pyridine. Although distd. at 20 mm., no b.p. was reported (1).]

3:9334 (1) Levene, Haller, *J. Biol. Chem.* **83**, 595 (1929).

3:9336 *cis*-1-CHLOROHEXENE-3 $C_6H_{11}Cl$ Beil. S.N. 11



B.P. 59–61° at 60 mm. (1) D_4^{24} = **0.900 (1)** n_D^{24} = **1.435 (1)**

Two geometrical stereoisomers of this structure are theoretically possible, but only that with the *cis* configuration ($\bar{C}$) has as yet been recognized.

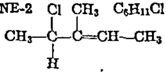
[For prepn. of $\bar{C}$ from *cis*-hexen-3-ol-1 [Beil. I_1-(229), I_2-(486)] (1) (2) (b.p. 156.1° at 760 mm. (3), 63.3° at 14 mm. (3), $D_4^{21.6}$ = 0.8478 (2), n_D^{24} = 1.4373 (2), 3,5-dinitrobenzoate, m.p. 44.5–46°, *N*-(α-naphthyl)carbamate, m.p. 80° (4)) with $SOCl_2$ + pyridine in $CHCl_3$ (72% yield (1)) see (1).]

$\bar{C}$ with NaI htd. 12 hrs. in acetone yields (1) 1-iodohexene-3, b.p. 62–63° at 12 mm., D_4^{21} = 1.469 (1).

$\bar{C}$ fails to react with activated Mg in dry ether, but the corresponding iodo cpd. (see above) yields the corresp. RMgI (1), and a mixt. of both can be used (5).

3:9336 (1) Ruzicka, Schinz, *Helv. Chim. Acta* **17**, 1606 (1934). (2) Stoll, Rouvé, *Helv. Chim. Acta* **21**, 1542–1547 (1938). (3) von Rechenberg, *J. prakt. Chem.* (2) **101**, 120 (1920). (4) van Romburgh, *Proc. Acad. Sci. Amsterdam* **22**, 758–761 (1920); *C.A.* **14**, 2780 (1920). (5) Stoll, Bolle, *Helv. Chim. Acta* **21**, 1551 (1938).

3:9338 *d,l*-4-CHLORO-3-METHYLPENTENE-2 $C_6H_{11}Cl$ Beil. I —
(α,β,γ-Trimethylallyl chloride) I_1-(90)
I_2—



B.P. 41–43° at 31 mm. (1)

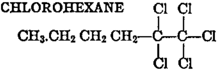
Note: although the product is as yet unrecognized, $\bar{C}$ by virtue of allylic transposition may conceivably be in equilibrium with its synionic isomer 2-chloro-3-methylbutene-3.

[For prepn. of $\bar{C}$ (75–80% yield (1)) from 3-methylpenten-2-ol-4 [Beil. I-445] by distn. with 6 *N* HCl see (1).]

$\bar{C}$ with quinoline at 170° loses HCl giving (66% yield (1)) 3-methylpentadiene-1,3 [Beil. I_1-(118), I_2-(231)], b.p. 76°.

3:9338 (1) Abelmann, *Ber.* **43**, 1579, 1583 (1910).

3:9328 1,1,1,2,2-PENTACHLOROHEXANE $C_6H_9Cl_5$ **Beil. S.N. 10**

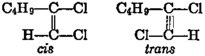


B.P. 129–131° at 10 mm. (1) **D^{25}_{-} = 1.370 (1)** **n^{25}_D = 1.4980 (1)**

[For formn of $\bar{C}$ from hexyne-1 (*n*-butylacetylene) (1:8055) with Cl_2 in MeOAc at 45° (1) or in 35% aq. HCl, 30% aq H_2SO_4, 30% aq. H_3PO_4, or 22% MeOH/HCl (2) (together with other products) see indic. refs.]

3:9328 (1) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460–1461 (1939). (2) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449–450 (1940).

3:9330 1,2-DICHLOROHEXENE-1 $C_6H_{10}Cl_2$ **Beil. S.N. 11**



cis *trans*

cis form

B.P. 88° at 30 mm. (1)	**D^{25}_4 = 1.0812 (1)**	**n^{25}_D = 1.4631 (1)**
80–82° at 25 mm. (2)	**D^{25}_{-} = 1.076 (2)**	**1.4629 (2)**

trans form

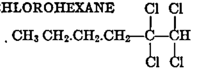
B.P. 63–65° at 32 mm. (1)	**D^{25}_4 = 1.1167 (1)**	**n^{25}_D = 1.4576 (1)**
55–57° at 25 mm. (2)	**D^{25}_{-} = 1.051 (2)**	**1.4543 (2)**

[For prepn. of $\bar{C}$ (*cis* form) from 2-chlorohexene-1 (3·7530) with Cl_2 in CCl_4 at 35–40° (1) (yield 26.7% together with 25 4% of 1,1,2,2-tetrachlorohexane (3:9332)) (1) or in Ac_2O, or AcOH (2), see indic. refs.; for prepn. of $\bar{C}$ (*trans* form) from hexyne-1 (1:8055) with Cl_2 in CCl_4 or heptane in pres. of trace of $SbCl_5$ (yield 19 6% together with 30.6% yield of 1,1,2,2-tetrachlorohexane (3 9332)) (1) or in aq. or *ter*-BuOH (2) see indic. refs.; for prepn. of $\bar{C}$ (both forms) from hexyne-1 (1:8055) + Cl_2 in conc. HCl, 30% H_2SO_4, 30% H_3PO_4, or MeOH satd. with HCl (together with other prods.) see (3) (4) or in MeOAc see (2).]

Neither *cis* nor *trans* forms of $\bar{C}$ will add HCl even in pres. of $BiCl_3$ (1) (3).

3:9330 (1) Hennion, Welsh, *J. Am. Chem. Soc.* **62**, 1367–1368 (1940). (2) Norris, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1460–1461 (1939) (3) Norris, Hennion, *J. Am. Chem. Soc.* **62**, 449–450 (1940) (4) Verbanc, Hennion, *J Am. Chem. Soc.* **60**, 1711–1713 (1938).

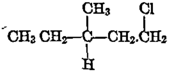
3:9332 1,1,2,2-TETRACHLOROHEXANE $C_6H_{10}Cl_4$ **Beil. S.N. 10**



B.P. 99–101° at 14 mm. (1)	**D^{25}_4 = 1.3096 (1)**	**n^{25}_D = 1.4888 (1)**
108–110° at 10 mm. (1)	**D^{25}_{-} = 1.320 (2)**	**1.4890 (2)**

[For formn. of $\bar{C}$ from hexyne-1 (*n*-butylacetylene) (1:8055) with Cl_2 in aq., MeOAc, Ac_2O, or AcOH at 45° (1), or in 35% aq. HCl, 30% aq H_2SO_4, 30% aq. H_3PO_4, or 22% MeOH/HCl (3), or in CCl_4 + $SbCl_5$ (30 6% yield (1)) (together with other products) see indic. refs.; for formn. of $\bar{C}$ from 2-chlorohexene-1 (3:7530) with Cl_2 in C_6H_6 + $BiCl_3$ at 35–40° (25.4% yield $\bar{C}$ + 26.7% yield *cis* 1,2-dichlorohexene-1 (3:9330)) see (1).]

3:9348 ***d,l*-1-CHLORO-3-METHYLPENTANE** $C_6H_{13}Cl$ **Beil. S.N. 10**

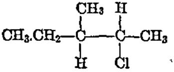


$\bar{C}$ itself seems to be unreported.

[The dextrorotatory isomer of $\bar{C}$ has, however, been studied (1) (2) (3). For prepn. of it from dextrorotatory 3-methylpentanol-1 with $SOCl_2$ see (1); b.p. 73° at 100 mm. (1), $D_4^{27} = 0.892$, $n_D^{25} = 1.4210$ (1). — With Mg in dry ether this isomer yields (2) (3) RMgCl which with CO_2 gives (2) (3) dextrorotatory 3-methylhexanoic acid-6, b.p. 115° at 16 mm. (2) (3), $D_4^{22} = 0.923$ (3).]

3:9348 (1) Levene, Marker, *J. Biol. Chem.* **91**, 86 (1931). (2) Levene, Marker, *J. Biol. Chem.* **95**, 11 (1932). (3) Levene, Marker, *J. Biol. Chem.* **95**, 161 (1932).

3:9350 ***d,l*-2-CHLORO-3-METHYLPENTANE** $C_6H_{13}Cl$ **Beil. S.N. 10**
(*sec.*-Butyl-methyl-carbinyl chloride)



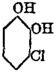
B.P. 71.1–73.3° at 160 mm. (1)

[For formn. of $\bar{C}$ (together with other products) in reaction of 2-ethylbutanol-1 (1:6223) with HCl + $ZnCl_2$ see (1)].

$\bar{C}$ with Mg + dry ether yields (1) RMgCl which with O_2 yields (1) 3-methylpentanol-2 (1:6202); this alc. upon oxidn. with CrO_3/H_2SO_4 yields (1) 3-methylpentanone-2 (2,4-dinitrophenylhydrazone, m.p. 71.2° (2), 70.5–72.5° (1)).

3:9350 (1) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2535 (1938). (2) Drake, Veitch, *J. Am. Chem. Soc.* **57**, 2624 (1935).

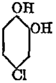
—— **3-CHLOROCATECHOL** $C_6H_5O_2Cl$ **Beil. VI —** **VI_1-(388)** **VI_2—**



B.P. 110–111° at 11 mm. **M.P. 47°**

See 3:0745. *Division A: Solids.*

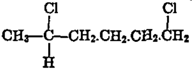
—— **4-CHLOROCATECHOL** $C_6H_5O_2Cl$ **Beil. VI - 783** **VI_1-(389)** **VI_2-(787)**



B.P. 139° at 10 mm. **M.P. 90–91°**

See 3:2470. *Division A: Solids.*

3:9340 ***d,l*-1,5-DICHLOROHEXANE** $C_6H_{12}Cl_2$ **Beil. I - 144**
I_1-(52)
I_2—

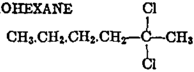


B.P. 74–78° at 10 mm. (1)

Heavy oil with agreeable odor. — Insol aq.
[For prepn. of C̄ (50% yield (1)) from *N*-benzoyl-2-methylpiperidine (*N*-benzoyl-α-pipecoline) [Beil XX-97] with PCl_5 (1), from hexanediol-1,5 [Beil. I-484] or the corresponding internal ether, 2-methyltetrahydropyran [Beil. XVII-13], by repeated treatment with HCl (2), or from hexamethylenediamine [Beil. IV-269] with NOCl (3) see indic. refs.]

3:9340 (1) von Braun, Sobecki, *Ber* **44**, 1042–1043 (1911). (2) Lipp, *Ber.* **18**, 3283–3286 (1885). (3) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 606–632 (1898); *Cent.* **1899**, I 25.

3:9342 2,2-DICHLOROHEXANE $C_6H_{12}Cl_2$ **Beil. S.N. 10**

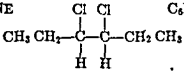


B.P. 68° at 49 mm. (1) D_4^{25} = **1.0150 (1)** n_D^{25} = **1.4353 (1)**

[For formn. of C̄ (40% yield (1) together with 20% yield (1) of 2-chlorohexene-1 (3:7530)) from hexyne-1 (1:8055) with HCl gas + $BiCl_3$ see (1).]
C̄ htd. at 95° with soln of solid KOH in *n*-propyl alc. gives (60.5% yield (1)) 2-chlorohexene-1 (3:7530).

3:9342 (1) Hennion, Welsh, *J. Am. Chem. Soc.* **62**, 1367–1368 (1940).

3:9344 3,4-DICHLOROHEXANE $C_6H_{12}Cl_2$ **Beil. S.N. 10**

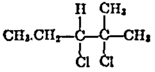


B.P. 69–70° at 30 mm. (1) D_-^{20} = **1.055 (1)** n_D^{20} = **1.4490 (1)**

Colorless liq. with sweetish odor.
[For prepn. of C̄ from hexene-3 (1:8270) with Cl_2 in $CHCl_3$ at −30° to −40° (67% yield (1)), or with SO_2Cl_2 at 40–50° (1), or with PCl_5 in CCl_4 (1) see (1).]

3:9344 (1) Spiegler, Tinker, *J. Am. Chem Soc.* **61**, 941–942 (1939).

3:9346 ***d,l*-2,3-DICHLORO-2-METHYLPENTANE** $C_6H_{12}Cl_2$ **Beil. I —**
I_1—
I_2-(111)



B.P. 82–84° at 42 mm. (1)

[For formn. of C̄ from 2-methylpentene-2 (1:8275) with Cl_2 in $CHCl_3$ (some 2-(or 3)-chloro-2-methylpentane (3:7490) is also formed) see (1).]

3:9346 (1) van Risseghem, *Bull. soc. chim. Belg.* **32**, 140–150 (1923).

Cryst. pdr. from C_6H_6 + lt. pet. (1). — Sol. ether, $CHCl_3$, C_6H_6; insol. aq.

[For prepn. of C̄ from β-naphthoic acid (1:0800) with PCl_5 (2) (3) or with $SOCl_2$ (100% yield (4)) (1) (5) see indic. refs.]

C̄ with *ter* bases + $K_2S_2O_5$ (6) or C̄ with calcium β-naphthoate at 150–160° (7) yields β-naphthoic acid anhydride, m.p. 134° (7) [cf. α-naphthoyl chloride (3:6930)].

[illegible] yields corresp. β-naphthyl ketones: e g., with biphenyl [illegible] ,3- *(10)*, 2,6- *(11)*, *and* 2,7- *(12)* dimethylnaphtha- [illegible] with RMgX cpds. also yields β-naphthyl ketones; e.g., see (14).]

[For use of C̄ in prepn. of vat dyes from mono- and diamino-anthraquinones see (15).]

C̄ with hydrazine hydrate yields (5) both β-naphthoylhydrazine (β-naphthoylhydrazide), cryst. from alc., m.p. 147.5° (5), and *N,N'-bis*-(β-naphthoyl)hydrazine, cryst. from AcOH, m.p. 241° (5).

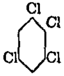
C̄ on hydrolysis yields β-naphthoic acid (1:0800), m.p. 184°. — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see β-naphthoic acid (1:0800); in addition see below.

Ⓓ β-Naphthoic β-naphthalide: ndls. from hot $CHCl_3$, m.p. 238° (4). [From C̄ + β-naphthylamine in C_6H_6 (4).]

3:0900 (1) Bell, *J. Chem. Soc.* **1930**, 1985. (2) Vieth, *Ann.* **180**, 317–319 (1875). (3) Raiford, [illegible] *Ber.* **56**, 352 [illegible] *Praktika* [illegible] (1876). (8) de Ceuster, *Cent.* **1932**, II 1290. (9) Clar, [illegible] *J. Chem. Soc.* **1933**, 1596.

(11) Fieser, Dietz, *Ber.* **62**, 1831 (1929). (12) Cook, *J. Chem. Soc.* **1931**, 492. (13) Migita, *Bull. Chem. Soc. Japan* **7**, 379 (1932). (14) Fieser, Seligman, *J. Am. Chem. Soc.* **58**, 478–480 (1936). (15) Meyer, Hopff (to I.G.), Ger. 432,579, Aug. 7, 1926; *Cent.* **1926**, II 2231.

3:0915 1,2,3,5-TETRACHLOROBENZENE



$C_6H_2Cl_4$ Beil. V - 204
V_1-(113)
V_2-(157)

M.P. 51°	(1) (2) (3)	B.P. 246° cor. (5)
50.5–51.0°	(4)	
50.3–51.3°	(6)	
50–51°	*(5) (7)*	
49°	(8)	

Ndls. from alc. — Spar. sol. cold alc.; eas. sol. C_6H_6, very eas. sol. CS_2 or lgr. — Volatile with steam.

[For prepn. of C̄ from 2,4,6-trichloroaniline [Beil. XII-627, XII_1-(312)] via diazotization [illegible] 55.8% (2))

via tetrazotization and warming with Cu_2Cl_2 see (7); for formn. of C̄ from [illegible] (3:0980) with $AlCl_3$ + S_2Cl_2 in SO_2Cl_2 at 40° (10% pure C̄ + 67% 1,2,4,5-tetrachlorobenzene (3:4115)) see (1); from [illegible] with PCl_3 + PCl_5 in s.t. at 200–300° see Beil. V-204; fr[illegible] e (10) or 2,5-dichlorobenzene-1,3-*bis*-(sulfo[illegible] -(sulfonyl chloride) (4) on htg. in s.t. with PCl_5 see indic. refs.; for formn. of C̄ from 1,3,5-trichloro-

3:9351 DIMETHYL CHLOROMALEATE $C_6H_7O_4Cl$ Beil. II —
II₁-(305)
II₂-(646)

$$\begin{array}{l} Cl—C—COOCH_3 \\ \quad\ \ \| \\ H—C—COOCH_3 \end{array}$$

B.P. 106.5° cor. at 18 mm. (1)	$D^{25}_{4vac.} = 1.2775$ (1)		
100° at 17 mm. (2)	$D^{20}_{4} = 1.276$ (2)	$n^{20}_{He} = 1.461$	(2)
	$D^{18.9}_{4} = 1.2775$ (2)	$n^{18.9}_{He} = 1.46170$	(2)

[For prepn. of C̄ from chloromaleic anhydride (3:0280) with abs. MeOH + conc. H_2SO_4 in cold see (2).]

3:9351 (1) Walden, Swinne, *Z. physik. Chem.* **79**, 741 (1912). (2) von Auwers, Harres, *Ber.* **62**, 1681, 1686–1687 (1929).

3:9352 ADIPYL (DI)CHLORIDE $C_6H_8O_2Cl_2$ Beil. II - 653
II₁-(277)
II₂-(575)

$$\begin{array}{ccc} O{=}C—(CH_2)_4—C{=}O \\ | \qquad\qquad\quad | \\ Cl \qquad\qquad\ \ Cl \end{array}$$

B.P. 130–132° at 18 mm., sl. dec. (1)
125–128° at 11 mm., sl. dec. (1)
125° at 11 mm. (2)
83–85° at 1 mm. (3)

[For prepn. of C̄ from adipic acid (1:0775) with PCl_5 (5) (yield: 79% (4), 50% (1)), with PCl_3 (5) (82% yield (6)), with $PCl_3 + ZnCl_2$ (76% yield (4)), or with $SOCl_2$ (yield: 100% (2), 90% (3), 81% (4), 60% (7)) (8) (9) (10) (19) see indic. refs.]

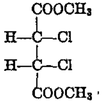
[For study of reactn. of C̄ with Cl_2 see (11); of C̄ with Br_2 see (11) (12) (13) (19); with diethyl sodio-malonate see (14); with MeZnI or EtZnI see (7); with triethylamine or with pyridine in C_6H_6 see (15).]

[C̄ with $AlCl_3 + C_6H_6$ gives (75–81% yield (9)) (8) (1) (6) (16) 1,6-diphenylhexanedione-1,6 (dibenzoylbutane) [Beil. VII-777, VII₁-(404)], cryst. from alc., m.p. 106–107° (9), 107° (6) (16) (note that some δ-benzoyl-*n*-valeric acid [Beil. X₁-(339)], m.p. 78° (16) 77–78° (17) (*p*-nitrophenylhydrazone, m.p. 187° (17), semicarbazone, m.p. 187° (17)), is, also formed). — For reactn. of C̄ with $AlCl_3$ + toluene, *m*-xylene, *p*-xylene, mesitylene, (18) or chlorobenzene (8) see indic. refs.]

C̄ on hydrolysis yields adipic acid (1:0775) (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to C̄ see 1:0775).

3:9352 (1) Etaix, *Ann. chim.* (7) **9**, 369–377 (1896). (2) Fröschl, Maier, *Monatsh.* **59**, 271–272 (1932). (3) Lieser, Macura, *Ann.* **548**, 226–254 (1941). *C.A.* **37**, 4699 (1943). (4) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (5) Ruggli, *Ann.* **399**, 179–180 (1913). (6) Borsche, Wollemann, *Ber.* **45**, 3715–3716 (1912) (7) Blaise, Koehler, *Bull. soc. chim.* (4) **5**, [illegible]

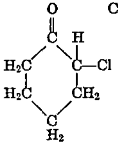
— DIMETHYL *d,l*-α,α'-DICHLOROSUCCINATE $C_6H_8O_4Cl_2$ Beil. II — II_1-(267) II_2-(557)



B.P. 116.5–120.5° cor. at 12.5 mm. **M.P. 43°**

See 3:0485. *Division A: Solids.*

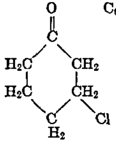
— 2-CHLOROCYCLOHEXANONE C_6H_9OCl Beil. VII - 10 VII_1-(8)



B.P. 88–90° at 16 mm. **M.P. 23–24°** $D_{15}^{20} = 1.161$ $n_D^{20} = 1.4825$

See 3:0120. *Division A: Solids.*

3:9360 3-CHLOROCYCLOHEXANONE C_6H_9OCl **Beil. VII- 10**

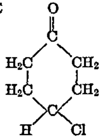


B.P. 91–92° at 14 mm. (1).

Colorless oil. — $\bar{C}$ does *not* fume in air or attack skin (1).
[For prepn. from cyclohexen-1-one-3 + dry HCl in dry ether see (1).]

3:9360 (1) Kötz, Grethe, *J. prakt. Chem* (2) **80**, 503–504 (1909).

3:9364 4-CHLOROCYCLOHEXANONE C_6H_9OCl **Beil. S.N. 612**



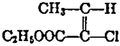
B.P. 95° at 17 mm. (1) $n_D^{20} = 1.4867$ (1)

Liq. with penetrating odor (1).
[For prepn. from 4-chlorocyclohexanol-1 (3:9376) by oxidn. with CrO_3 see (1) (3).]

Ⓓ 4-Chlorocyclohexanone-1 semicarbazone: from C̄ + semicarbazide HCl + KOAc (1); cryst. from aq., m p. 191° (block) (1); 196° (2).

3:9364 (1) Sabetay, Palfray, *Bull. soc. chim.* (4) **43**, 909 (1928). (2) Palfray, Rothstein, *Compt. rend* **190**, 944 (1930). (3) Backer, Tamsma, *Rec. trav. chim.* **57**, 1205–1206 (1938).

3:9368 ETHYL α-CHLOROISOCROTONATE $C_6H_9O_2Cl$ Beil. II —
II_1—
II_2-(396)



B.P. 75° at 30 mm. (1) D_4^{20} = 1.100 (1) n_{He}^{20} = 1.4530 (1)
58° at 12 mm. (1) D_4^{18} = 1.1021 (1)

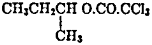
[*See also ethyl α-chlorocrotonate* (3:8523).]

[For prepn. of C̄ from Ag salt of α-chloroisocrotonic acid (3:1615) with C_2H_5I see (1); note that attempts to prepare C̄ from α-chloro-isocrotonic acid (3:1615) in EtOH with conc. H_2SO_4 at 100° give only (1) the stereoisomeric ethyl α-chlorocrotonate (3:8523).]

C̄ with alc. KOH at room temp. gives upon acidification α-chloroisocrotonic acid (3:1615), m p. 66°.

3:9368 (1) von Auwers, *Ann.* **432**, 61–62 (1923)

3:9372 *sec.*-BUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. S.N. 160



B.P. 88–89° at 19 mm. (1) D_4^{25} = 1.252 (1) n_D^{25} = 1.4440 (1)

[For prepn. (82–89% yield) from butanol-2 (1:6155) + trichloroacetic ac. (3:1150) see (1).]

[For study of chlorination of C̄ see (1).]

3:9372 (1) Waddle, Adkins. *J Am. Chem Soc.* **61**, 3361–3364 (1939).

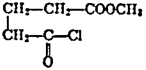
— *ter*-BUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. S.N. 160

$Cl_3C.CO\ O\ C_4H_9$

B.P. 37° at 1 mm. M.P. 25.5° D_4^{25} = 1.2363 n_D^{25} = 1.4398

See 3:0138. *Division A: Solids.*

3:9373 METHYL γ-(CHLOROFORMYL)-*n*-BUTYRATE $C_6H_9O_3Cl$ Beil. S.N. 172
(γ-(Carbomethoxy)-*n*-butyryl chloride)



B.P. 110° at 30 mm. (1)
110–113° at 23 mm. (5)
110° at 20 mm. (2)

Note that C̄ is both an acid chloride and an ester.

[For prepn. of $\bar{C}$ from methyl hydrogen glutarate [Beil. II_2-(565)] (b.p. 158° at 27 mm. (1), 153° at 20 mm. (2), 150–151° at 10 mm. (3), $D^{18}_{-} = 1.164$ (3), $n^{18}_{D} = 1.4392$ (3), itself obtd. from glutaric anhydride with MeOH (2) (1)) with $SOCl_2$ at 20° for 12 hrs., then at 30° for 3 hrs. (yield 93% (1), 87% (5)) (2), see indic. refs.]

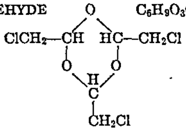
[For behavior of $\bar{C}$ with EtMgI in toluene followed by hydrolysis giving δ-keto-*n*-heptanoic acid, m.p. 50° see (2); for reaction of $\bar{C}$ with atoxyl see (1).]

[For use of $\bar{C}$ in Friedel-Crafts type of reaction see (4).]

[$\bar{C}$ on catalytic hydrogenation as directed gives (70–85% yield (5)) methyl γ-formyl *n*-butyrate, b.p. 100–103° at 23 mm. (corresp. 2,4-dinitrophenylhydrazone, m.p. 105–106°) (5).]

3:9373 (1) Morgan, Walton, *J. Chem. Soc* **1932**, 277. (2) Clutterbuck, Raper, *Biochem. J.* **19**, 393–394 (1925). (3) Fourneau, Sabetay, *Bull. soc. chim.* (4) **45**, 838–839 (1929). (4) Robinson, Walker, *J. Chem. Soc.* **1937**, 62, 66–67. (5) Harris, Wolf, Mozingo, Arth, Anderson, Easton, Folkers, *J. Am. Chem. Soc.* **67**, 2098 (1945).

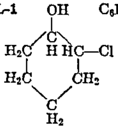
—— TRICHLOROPARALDEHYDE $C_6H_9O_3Cl_3$ Beil. XIX - 386 XIX_1-(807)



B.P. 142° at 10 mm. **M.P. 87–87.5° cor.**

See 3:2300. *Division A: Solids*

3:9374 *cis*-2-CHLOROCYCLOHEXANOL-1 $C_6H_{11}OCl$ Beil. S.N. 502
(*cis*-Cyclohexene chlorohydrin)



B.P. 93–94° at 26 mm. (1)	$D^{25}_{-} = 1.1261$ (1)	$n^{25}_{D} = 1.4860$ (1)
76° at 15 mm. (2)	$D^{15}_{-} = 1.150$ (2)	$n^{15}_{D} = 1.4860$ (2)

[*See also trans-2-chlorocyclohexanol*-1 (3:0175).]

[For prepn. of $\bar{C}$ from 2-chlorocyclohexanone-1 (3:0120) by reductn. with isopropyl MgCl, *ter*-butyl MgX, or cyclohexanyl MgX (the prod. is actually a mixt. of $\bar{C}$ (72–73%) with the *trans* isomer (27–28%) see (1); for formn. of $\bar{C}$ from cyclohexene (1:8070) with HOCl see (2) cf. (5) (this method is claimed by (2) to yield some $\bar{C}$, but according to (1) gives solely the *trans* isomer).]

$\bar{C}$ with aq. NaOH gives on refluxing (76% yield (1)) cyclohexanone (1:5465) (note difference from the *trans* isomer which gives cyclohexene oxide). — $\bar{C}$ with conc. HCl or with $ZnCl_2$ in ether shows no tendency to convert to the *trans* isomer (1).

(Note: the following derivatives are listed as *trans* on the assumption of inversion during formation.)

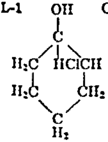
—— *trans*-2-Chlorocyclohexanyl acetate: consts. not reported (4).

—— *trans*-2-Chlorocyclohexanyl *N*-phenylurethane: m.p. 56–59° (3). [From C̄ + phenyl isocyanate in lt. pet. (3).]

—— *trans*-2-Chlorocyclohexanyl *N*-(α-naphthyl)carbamate: m.p. 165° (1). [From C̄ with α-naphthyl isocyanate htd. 4 hrs. at 100° (1).]

3:9374 (1) Bartlett, *J. Am. Chem. Soc.* **57**, 224–227 (1935). (2) Godchot, Mousseron, Granger, *Compt. rend.* **200**, 748–749 (1935). (3) Cook, Hewitt, Lawrence, *J. Chem. Soc.* **1936**, 75. (4) Winstein, Buckles, *J. Am. Chem. Soc.* **65**, 616 (1943). (5) Newman, Van der Werf, *J. Am. Chem. Soc.* **67**, 235 (1945).

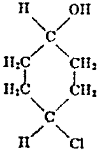
—— *trans*-2-CHLOROCYCLOHEXANOL-1 $C_6H_{11}OCl$ Beil. VI - 7
VI₁—
VI₂-(12)



B.P. 104–106° at 45 mm. M.P. 29° D_{-}^{15} = 1.140 n_D^{15} = 1.4850

See 3:0175. *Division A: Solids.*

3:9376 4-CHLOROCYCLOHEXANOL-1 $C_6H_{11}OCl$ Beil. VI —
(Quinitol chlorohydrin) VI₁—
VI₂-(12)



B.P. 100° at 14 mm. (1) D_4^{17} = 1.1435 (2) n_D^{17} = 1.4930 (2)
105° at 12 mm. (2)

Colorless oil.

[For prepn. from quinitol (cyclohexanediol-1,4) {Beil. VI-741} by htg. with conc. HCl see (1) (2); for formn. from resorcitol (cyclohexanediol-1,3) {Beil. VI-740} with conc. HCl see (3).]

[C̄ on refluxing 2 days in dry ether with Na yields (3) (by loss of HCl and rearr.) cyclohexen-3-ol-1, b.p. 67–68° at 14 mm., D_4^{23} = 0.9125, n_D^{23} = 1.4627; *N*-phenylcarbamate, m.p. 82° (block) (1).] — [C̄ with powd. KOH in ether is only partially transformed to cyclohexen-3-ol-1, even on boiling (1).]

C̄ on oxidn. with CrO_3 yields (1) (3) 4-chlorocyclohexanone-1 (3:9364).

[The acetyl deriv. of C̄ is an oil, b.p. 111–112° cor. at 18 mm., $D_4^{15.4}$ = 1.1282, $n_D^{15.4}$ = 1.4629 (2).]

D 4-Chlorocyclohexyl *N*-phenylcarbamate: m.p. 99° (2).

3:9376 (1) Sabetay, Palfray, *Bull. soc. chim.* (4) **43**, 908–910 (1928). (2) Palfray, Rothstein, *Compt. rend.* **189**, 701–703 (1929). (3) Palfray, Rothstein, *Compt. rend.* **190**, 942–943 (1930).

3:9380 *n*-AMYL CHLOROFORMATE $C_6H_{11}O_2Cl$ Beil. S.N. 199
(*n*-Amyl chlorocarbonate) *n*-C_5H_{11} O.CO.Cl

B.P. 60–62° at 15 mm. (1) n_D^{18} = **1.4181** (2)
53.4–54.5° at 11 mm. (2)

$\bar{C}$ on htg. with quinoline dec. at 72° (3) into *n*-amyl chloride (3:7460) + CO_2; $\bar{C}$ on htg with $ZnCl_2$ gives these + amylene (and its polymers) + HCl (4).

3:9380 (1) Eastman Organic Chemicals, List No. 36 (1946). (2) Kohlrausch, Sabathy, *Monatsh.* **72**, 307 (1939). (3) Carré, *Bull soc. chim.* (5) **3**, 1069 (1936). (4) Underwood, Baril, *J. Am Chem. Soc.* **57**, 2729 (1935).

3:9384 *n*-PROPYL *d,l*-α-CHLOROPROPIONATE $C_6H_{11}O_2Cl$ Beil. S.N. 162

$$n\text{-}C_3H_7.O.CO\,\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}.CH_3$$

B.P. — D_4^{20} = **1.0478** (1) n_D^{20} = **1.4218** (1)

3:9384 (1) Schjanberg, *Z. physik. Chem.* **A-172**, 230 (1935).

3:9388 ISOPROPYL β-CHLOROPROPIONATE $C_6H_{11}O_2Cl$ Beil. S.N. 162
$(CH_3)_2CH$ O $CO.CH_2$ CH_2Cl

B.P. — D_4^{20} = **1.0503** (1) n_D^{20} = **1.4230** (1)

3:9388 (1) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

3:9390 β-(β-HYDROXYETHOXY)ETHYL CHLOROACETATE Beil. S.N. 160
(Diethylene glycol mono(chloroacetate)) $C_6H_{11}O_4Cl$
$HOCH_2.CH_2.O.CH_2$ CH_2 $O.CO.CH_2Cl$

B.P. 130–142° at 0.2 mm. (1)

Viscous oil, insol in aq. but slowly dissolving when shaken with aq. because of hydrolysis to diethylene glycol (1:6525) + chloroacetic ac. (3:1370) (1).

3:9390 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 317 (1933).

3:9394 FORMALDEHYDE β,β′-DICHLORO-ISOPROPYL-ETHYL-ACETAL $C_6H_{12}O_2Cl_2$ Beil. I —
$(ClCH_2)_2CH.O.CH_2.O.C_2H_5$ I_1—
(β,β′-Dichloroisopropyl-ethyl-formal) I_2-(640)

B.P. 96–98° at 16 mm. (1) D_{17}^{17} = **1.182** (2) n_D^{17} = **1.44912** (2)
90–91° at 12 mm. (2)

Colorless liq. with ethereal odor.
[For prepn. of $\bar{C}$ from epichlorohydrin (3-chloro-1,2-epoxypropane) (3:5358) + chloromethyl ethyl ether (3:7195) see (1) (2).]

3:9394 (1) Blanchard, *Bull. soc. chim.* (4) **39**, 1265 (1926). (2) Blanchard, *Bull. soc. chim.* (4) **49**, 285 (1931).

3:9395 6-CHLOROHEXANOL-1 $CH_2.(CH_2)_4\,CH_2OH$ (with Cl on the first CH_2) $C_6H_{13}OCl$ **Beil. S.N. 24**
(ω-Chloro-*n*-hexyl alcohol)

B.P. 116–117° at 19 mm. (1)
112° at 17 mm. (1)

[For prepn of C̄ from α,ω-hexamethylene glycol [Beil. I-484, I_1-(251), I_2-(551)] (b p 145–149° at 18 mm. (2)) with conc. HCl as directed (1) cf. (2) (yields: 65% (3)) see indic. refs.]

[C̄ with KSEt in alc. htd. ½ hr. gives (1) ethyl 6-hydroxy-*n*-hexyl sulfide, colorless oil, b p. 134–136° at 17 mm.; this prod with $SOCl_2$ + diethylaniline in CCl_4 at 55° gives (1) 6-chloro-*n*-hexyl ethyl sulfide, b.p. 128–131° at 26 mm.]

C̄ with thiophenol has not been studied [however, 6-chloro-*n*-hexyl acetate with excess thiophenol in aq. NaOH htd 3 hrs. gives (85% yield (2)) 6-hydroxy-*n*-hexyl phenyl sulfide, pl from lt. pet., m.p. 43°; this prod. with $SOCl_2$ + diethylaniline in CCl_4 yields (2) 6-chloro-*n*-hexyl phenyl sulfide, m.p. 7–8° (undistillable)]

[C̄ (1 mole) with Et_2NH (2 moles) in s.t. at 100° for 16 hrs gives (58% yield (4)) 6-(diethylamino)hexanol-1, b.p. 96–99° at 2 mm. (4), this prod with $SOCl_2$ in $CHCl_3$ gives (39% yield (4)) 6-(diethylamino)-*n*-hexyl chloride, b.p. 118–120° at 19 mm]

C̄ with morpholine gives (5) alm. quant. 6-(4-morpholinyl)hexanol-1, b p. 146 0–147.0° at 5 mm., $D_4^{25} = 0.9884$, $n_D^{25} = 1.4750$ (corresp *N*-(α-naphthyl)carbamate, m.p 71.0–72 0° cor.) (5). — C̄ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs gives (3) in alm. 100% yield (as salt) *N*-(6-hydroxy-*n*-hexyl)-*N'*-phenylpiperazine, m.p. 65.5–67.0° cor. (corresp. *N*-phenylcarbamate, m p. 91.5–93.0° cor) (3).

——**6-Chloro-*n*-hexyl acetate:** oil, b.p 113–116° at 17 mm [Prepd. indirectly (2)]
Ⓓ **6-Chloro-*n*-hexyl *N*-phenylcarbamate:** m.p 49–50° (3).

3:9395 (1) Bennett, Turner, *J. Chem. Soc* **1938**, 813–815 (2) Bennett, Mosses, *J. Chem. Soc.* **1931**, 1698–1699. (3) Anderson, Pollard, *J Am. Chem. Soc.* **61**, 3439–3440 (1939). (4) Work, *J. Chem. Soc.* **1942**, 428. (5) Anderson, Pollard, *J. Am. Chem. Soc* **61**, 3440–3441 (1939).

3:9396 *n*-BUTYL α-CHLOROETHYL ETHER $CH_3\,CH(Cl)\,O\,n\text{-}C_4H_9$ $C_6H_{13}OCl$ **Beil. S.N. 78**
(α-Chloroethyl *n*-butyl ether)

B.P. 48.9–50.3° cor. at 11 mm. (1) $D_4^{20} = 0.9335$ **(1)** $n_D^{20} = 1.4155$ **(1)**

C̄ decomposes considerably if distd at ord. press. (2).

[For prepn. (95% yield (1)) from paraldehyde (1:0170) + *n*-butyl alc. (1:6180) + dry HCl see (1).]

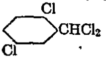
C̄ on stdg. polymerizes to dark tarry residue (1).

[C̄ on bromination yields α,β-dibromoethyl *n*-butyl ether (2).]

C̄ on shaking with aq yields acetaldehyde (1:0100), *n*-butyl alc. (1:6180), + HCl.

3:9396 (1) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077–4079 (1931). (2) Dykstra, Lewis, Boord, *J. Am. Chem. Soc.* **52**, 3399–3400 (1930).

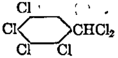
—— 2,5-DICHLOROBENZAL (DI)CHLORIDE $C_7H_4Cl_4$ Beil. V - 302
V₁—
V₂-(234)



B.P. 118–120° at 14 mm. M.P. 43°

See 3:0490. *Division A: Solids.*

3:9397 2,3,4,5-TETRACHLOROBENZAL (DI)CHLORIDE $C_7H_2Cl_6$ Beil. S.N. 466



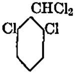
No physical constants on C̄ are available.

[For prepn. of C̄ from 2,3,4,5-tetrachlorotoluene (3:2710) with Cl_2 see (1).]

C̄ on hydrolysis (presumably with strong H_2SO_4) gives (1) 2,3,4,5-tetrachlorobenzaldehyde (3:3140).

3:9397 (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; *Cent.* **1926**, II 2355; *C.A.* **21**, 1361 (1927); French 603,650, April 26, 1926; *Cent.* **1926**, II 2355; not in *C.A.*

3:9398 2,6-DICHLOROBENZAL (DI)CHLORIDE $C_7H_4Cl_4$ Beil. V - 302
V₁—
V₂—



B.P. 124–126° at 16 mm. (1)

Oil with penetrating odor.

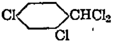
[For prepn. of C̄ from 2,6-dichlorobenzaldehyde (3:1690) with PCl_5 (90% yield (1)) (2) (note the intermediate formn. of *bis*-(α,2,6-trichlorobenzyl) ether (2)) or from 2,6-dichlorotoluene (3:6270) with Cl_2 (4) see indic. refs.]

C̄ is extremely resistant to hydrolysis with either acid or alkali or conc. H_2SO_4; for details see (3) (5).

[For condens. of C̄ with various phenols (e.g., 2,4-dichlorophenol (3:0560)) in prepn. of mothproofing agts. see (6).]

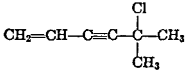
3:9398 (1) [illegible] -*him.* **52**,
[illegible] gy, Ger.
[illegible] (1933).
[illegible] 4, 1930;
French 39,334, Oct. 12, 1931, *Cent.* **1932**, I 3013.

3:9399 2,4-DICHLOROBENZAL (DI)CHLORIDE $C_7H_4Cl_4$ Beil. S.N. 466



This compound appears to be unreported. However, for many isomeric compounds see the Formula Index.

3:9402 5-CHLORO-5-METHYLHEXEN-1-YNE-3 C_7H_9Cl Beil. S.N. 13
(2-Chloro-2-methylhexen-5-yne-3; dimethyl-vinylethynyl-carbinyl chloride)



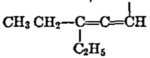
B.P. 48–49° at 28 mm. (1) $n_D^{15} = 1.4812$ (1)
31–32° at 10 mm. (1)

[For prepn. of $\bar{C}$ from dimethyl-vinylethynyl-carbinol (b.p. 58–59° at 13 mm, D_4^{15} = 0.8925, n_D^{15} = 1.4786 (2), see (1).]

[$\bar{C}$ with phenol + KOH in acetone refluxed 3 hrs. yields (3) about equal amts. of 2-methylhexadien-1,5-yne-3 (α-isopropenyl-β-vinyl-acetylene) + the phenyl ether of $\bar{C}$ (dimethyl-phenoxy-vinylethynyl-methane), b.p. 105.5° at 7 mm., D_4^{16} = 0.9714, n_D^{16} = 1.5350 (3).]

3:9402 (1) Nazarov, *Bull. acad sci. U.R.S.S., Classe sci. math. nat., Ser. chim.* **1938**, 695–705; *Cent.* **1939**, II 3403; *C.A* **33**, 5682 (1939). (2) Nazarov, *Bull. acad sci U.R.S.S., Classe sci. math. nat., Ser chim* **1938**, 683–694; *Cent.* **1939**, II 3402; *C.A.* **33**, 5682 (1939). (3) Nazarov, Elizarova, *Bull. acad sci. U.R.S.S., Classe sci. chim.* **1941**, 423–430; *C.A.* **36**, 1298 (1942).

3:9406 1-CHLORO-3-ETHYLPENTADIENE-1,2 $C_7H_{11}Cl$ Beil. S.N. 12



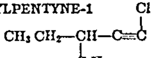
B.P. 85–88° at 100 mm. (1) $D_4^{18.5}$ = 0.9297 (1) $n_\alpha^{18.5}$ = 1.47036 (1)
$D_4^{16.5}$ = 0.9329 (1) $n_\beta^{18.5}$ = 1.48431 (1)

[For prepn. of $\bar{C}$ from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I_1-(236), I_2-(506)] (1) directly, or from the intermediate 1-chloro-3-ethylpentyne-1 (3:9410) by rearr., on shaking either with aq HCl contg. Cu_2Cl_2 + NH_4Cl (some 3-ethylpenten-3-yne-1 also being formed in the latter case) see (1).]

$\bar{C}$ with aq. + $CaCO_3$ first isomerizes to 1-chloro-3-ethylpentyne-1 (3:9410) which then yields 3-ethylpentyn-1-ol-3 (b.p. 136–137°, D_4^{17} = 0.8748; *N*-phenylcarbamate, m.p. 52–53° (1); allophanate, m.p. 130–131° (2)) and 3-ethylpenten-3-yne-1, b.p. 41–43° at 100 mm, D_4^{13} = 0.7733, n_α^{13} = 1.43962, n_β^{13} = 1.45224 (1).

3:9406 (1) T. A. Favorskaya, I. A. Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 451–460 (1940); *C.A.* **34**, 7844 (1940). (2) Locquin, Sung, *Bull. soc. chim.* (4) **35**, 601 (1924).

3:9410 1-CHLORO-3-ETHYLPENTYNE-1 $C_7H_{11}Cl$ Beil. S.N. 12



B.P. 73–76° at 100 mm. (1) $D_4^{18.5}$ = 0.9230 (1) $n_\alpha^{18.5}$ = 1.44372 (1)
D_4^0 = 0.9330 (1) $n_\beta^{18.5}$ = 1.45364 (1)

[For prepn. of $\bar{C}$ from 3-ethylpentyn-1-ol-3 (diethyl-ethynyl-carbinol) [Beil. I_1-(236), I_2-(506)] (1) on shaking with HCl alone, or with HCl + Cu_2Cl_2 + NH_4Cl (70% yield together in the latter case with a maximum of 25–30% 1-chloro-3-ethylpentadiene-1,2 (3:9406)) see (1).]

C̄ on shaking with HCl + Cu_2Cl_2 + NH_4Cl is partly converted to 1-chloro-3-ethylpentadiene-1.2 (3:9406) (some 3-ethylpenten-3-yne-1 also being formed), but without the HCl no action occurs (1).

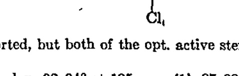
C̄ easily loses HCl yielding 3-ethylpenten-3-yne-1, b.p. 41–43° at 100 mm., D_4^{13} = 0.7733, n_α^{13} = 1.43962, n_β^{13} = 1.45224 (1).

C̄ upon hydrolysis (1) with aq. + $CaCO_3$ gives a mixt. of 3-ethylpentyn-1-ol-3 (b.p. 136–137°, D_4^{17} = 0.8748, n_α^{14} = 1.4385, n_β^{14} = 1.44697 (1) [*N*-phenylcarbamate, m.p. 52-53° (1), allophanate, m p. 130–131° (2)]) and 3-ethylpenten-3-yne-1 (see above).

3:9410 (1) T. A. Favorskaya, I. A. Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 451–460 (1940); *C.A.* **34**, 7844 (1940). (2) Locquin, Sung, *Bull. soc. chim.* (4) **35**, 601 (1924).

3:9412 ***d,l*-3-CHLOROHEPTENE-1** $C_7H_{13}Cl$ **Beil. S.N. 11**

(*n*-Butyl-vinyl-carbinyl chloride)



C̄ as such is as yet unreported, but both of the opt. active stereoisomerides have been prepared.

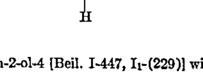
[The dextrorotatory isomer, b.p. 92–94° at 125 mm. (1), 87–88° at 90 mm. (1), D_4^{25} = 0.8857 (1), has been obtd. from levorotatory hepten-1-ol-3 (*n*-butyl-vinyl-carbinol) [Beil. I_2-(488)] with PCl_5 in dry ether (1), with PCl_3 + pyridine (2), or from levorotatory 3-bromoheptene-1 (1) with LiCl in MeOH (1).

[Upon ozonolysis in $CHCl_3$ followed by Br_2/aq. oxidn. of the resultant aldehyde, levorotatory α-chlorocaproic acid, b.p. 80–95° at 1 mm., was obtd. (2).]

[The levorotatory isomer, b.p. 87–90° at 92 mm. (3), D_4^{25} = 0.8883 (4), n_D^{25} = 1.4380 (4), has been obtd. from dextrorotatory hepten-1-ol-3 (*n*-butyl-vinyl-carbinol) (Beil. I_2-(488)] with PCl_5 (3); upon catalytic hydrogenation it yields (3) dextrorotatory 3-chloroheptane, b.p. 87–90° at 113 mm., n_D^{25} = 1.4221 (3); cf. *d,l*-isomer (3:8080).]

3:9412 (1) Levene, Rothen, Kuna, *J. Biol. Chem.* **120**, 787–790 (1937). (2) Levene, Haller, *J. Biol. Chem.* **83**, 597 (1929). (3) Levene, Rothen, *J. Biol. Chem.* **119**, 191–192 (1937). (4) Levene, Rothen, *J. Chem. Phys.* **5**, 981 (1937).

3:9414 4-CHLORO-3-METHYLHEXENE-2 $C_7H_{13}Cl$. Beil. I — I_1-(91) I_2—



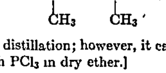
B.P. 51° at 11.5 mm. (1)

[For prepn. of C̄ from 3-methylhexen-2-ol-4 [Beil. I-447, I_1-(229)] with 6 *N* HCl see (1)].

3:9414 (1) Abelmann, *Ber.* **43**, 1581 (1910).

3:9418 4-CHLORO-2,4-DIMETHYLPENTENE-2 $C_7H_{13}Cl$ **Beil. S.N. 11**

(2-Chloro-2,4-dimethylpentene-3; trimethylcrotyl chloride)



[C̄ is too unstable for purification by distillation; however, it can be prepared in solution from 2,4-dimethylpenten-3-ol-2 (1) with PCl_3 in dry ether.]

benzene (3:1400) with Cl_2 in pres. of Al/Hg see (11); from benzene (12), chlorobenzene (13), or diphenyl sulfone (14) with Cl_2 followed by treatment with alc. KOH see indic. refs.]

[For behavior of C̄ with liq. Cl_2 yielding addn. products see (15).]

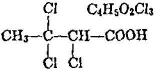
[For behavior of C̄ with NaOMe see (2) (16).]

C̄ on mononitration, e.g., by boilg. for ½ hr. with 3 pts. HNO_3 ($D = 1.52$) as directed (17), gives 96.7% yield (17) 1,2,3,5-tetrachloro-4-nitrobenzene, cryst. from spontaneous evapn. of alc. soln., m.p. 40–41° (17) (the m.p. of 21–22° previously reported (5) was on impure material).

C̄ on dinitration, e.g., by boilg. with a mixt. of 10 pts. fumg. HNO_3 ($D = 1.52$) + 4 pts. conc. H_2SO_4 for 1 hr. and then pouring into aq. (17), gives (100% yield (17)) (9) 1,2,3,5-tetrachloro-4,6-dinitrobenzene [Beil. V-266], pl. from 90% AcOH, m.p. 162° (9), 161–162° (17). (This prod. on htg. with aniline yields (9) (18) 2-chloro-1,3,5-trianilino-4,6-dinitrobenzene, crimson pl., m.p. 179° (9), 179–180° (18).)

3:0915 (1) Silberrad, *J. Chem. Soc.* **121**, 1020 (1922). (2) Holleman, *Rec. trav. chim.* **39**, 739, 749 (1920). (3) Willgerodt, Wilcke, *Ber.* **43**, 2752 (1910). (4) Olivier, *Rec. trav. chim.* **39**, 197 (1920). (5) Beilstein, Kurbatow, *Ann.* **192** 237–238 (1878) (6) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 433–434 (1932). (7) Schoutissen, *J. Am. Chem. Soc.* **55**, 4539 (1933) (8) Gebauer-Fulnegg, Figdor, *Monatsh.* **48**, 633–634 (1927). (9) Jackson, Carlton, *Ber.* **35**, [illegible] Molineus, *Ann* **415**, 62 (1918). [illegible] ati, *Ann. chim.* (6) **6**, 380, 384, [illegible] (14) Otto, Ostrop, *Ann.* **141**, 105 (1867). (15) van der Linden, *Rec. trav. chim.* **55**, 421–430 (1936). (16) de Crauw, *Rec. trav. chim.* **50**, 787 (1931). (17) Berckmans, Holleman, *Rec. trav. chim.* **44**, 852–856 (1925). (18) Qvist, Salo, *Acta Acad. Aboensis Math. et Phys.* 8, No 4 (1934), *Cent.* **1934**, II 595, *Cent.* **1936**, I 540.

3:0925 α,β,β-TRICHLORO-*n*-BUTYRIC ACID $C_4H_5O_2Cl_3$ Beil. II-281, II_1—, II_2—



M.P. 51.5–52° (1)

Tbls from lgr. — Spar. sol. aq., eas. sol. alc., ether, C_6H_6, $CHCl_3$, CS_2.

[For prepn. of C̄ from either β-chlorocrotonic acid (3:2625) or β-chloroisocrotonic acid (3:1300) in CS_2 soln. with Cl_2 stood several days in the dark see (1).]

[C̄ in aq. with granulated Zn stood for 6 weeks, then acidified, yields (1) mainly β-chloroisocrotonic acid (3:1300) *accompanied by some β-chlorocrotonic acid (3:2625); note that* former is separated from latter by its greater volatility with steam.]

C̄ with aq. Na_2CO_3 soln. on boilg. loses both HCl and CO_2 yielding the higher-boilg. (1) 1,2-dichloropropene-1 (3:5150).

C̄ with alc. KOH (2 moles) loses HCl yielding (1) mainly α,β-dichloroisocrotonic acid [Beil. II-418], m.p. 75.5°, accompanied by a little α,β-dichlorocrotonic acid [Beil. II-418], m.p. 92°; note that these are separated by the greater soly. of the former in lgr. (1).

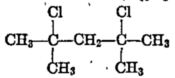
The acid chloride corresp. to C̄ is unreported.

—— Methyl α,β,β-trichloro-*n*-butyrate: unreported.
—— Ethyl α,β,β-trichloro-*n*-butyrate: unreported.
—— α,β,β-Trichloro-*n*-butyramide: unreported.
—— α,β,β-Trichloro-*n*-butyranilide: unreported.
—— α,β,β-Trichloro-*n*-butyr-α-naphthalide: unreported.

[For prepn. of C̄ from heptanone-4 (butyrone) (1:5447) with PCl_5 see (1); note that heptyne-3 (1:8095), b.p. 105–106°, and 4-chloroheptene-3 (3:8023) are also formed (1). The earlier prepns. are regarded as impure.]

3:9426 (1) Bourgeul, *Bull. soc. chim.* (4) **35**, 1636–1637 (1924). (2) Bourgeul, *Ann. chim.* (10) **3**, 372 (1925).

3:9428 2,4-DICHLORO-2,4-DIMETHYLPENTANE $C_7H_{14}Cl_2$ **Beil. S.N. 10**

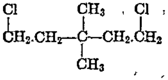


B.P. 51.5°, at 8 mm. (1)

[For study of behavior of C̄ with aq. alc. $N/10$ NaOH see (1).]

3:9428 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1380–1388 (1939); *C.A.* **34**, 1611 (1940).

3:9430 1,5-DICHLORO-3,3-DIMETHYLPENTANE $C_7H_{14}Cl_2$ **Beil. I —**
I_1—
I_2-(121)



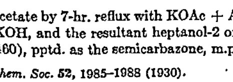
B.P. 135° at 80 mm. (1) **D_4^{15} = 1.0917 (2)** **n_D^{15} = 1.48990 (2)**
58–59° at 8 mm. (2)

[For prepn. of C̄ from 3,3-dimethylpentanediol-1,5 (1) with $SOCl_2$ refluxed for 4 hrs. (yield 80% (1)); from N-benzoyl-4,4-dimethylpiperidine (2) with PCl_5 see (2).]

[For reactn. of C̄ with alc. NaCN giving (yield: 80% (2), 40% (1)) 3,3-dimethylpimelonitrile, cryst. from C_6H_6/lgr., m.p. 123° (2), b.p. 155–157° at 7 mm. (1), D_{20}^{20} = 1.0936 (1), n_D^{20} = 1 4404 (1), see indic. refs.] [This dinitrile upon htg. with conc. HCl in s.t. 4 hrs. at 120° gives (85% yield (2)) γ,γ-dimethylpimelic acid; ndls. from C_6H_6/lgr., m.p. 83° (2) (diamide, m.p. 176° (2); dianilide, m.p. 165° (2)).]

3:9430 (1) Miller, Adams, *J. Am. Chem. Soc.* **58**, 789 (1936). (2) Komppa, *Ber.* **62**, 1371–1372 (1929).

3:9432 *d,l*-2-CHLOROHEPTANE $C_7H_{15}Cl$ **Beil. I-154**
(*n*-Amyl-methyl-carbinyl chloride) **I_1—**
I_2—



B.P. 46.0° at 19.5 mm. (1) **D_4^{20} = 0.8672 (1)** **n_D^{20} = 1.4221 (1)**
D_4^{15} = 0.8725 (1)

[For prepn. from heptanol-2 (1:6235) with conc. HCl + $ZnCl_2$ at 0° for 6–8 hrs. (60–64% yield (1)) see (1).]

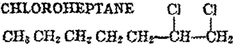
C̄ converted to corresp. acetate by 7-hr. reflux with KOAc + AcOH, then hydrolyzed by 6-hr. boilg. with 20% alc. KOH, and the resultant heptanol-2 oxidized with CrO_3/H_2SO_4, gives (1) heptanone-2 (1:5460), pptd. as the semicarbazone, m.p. 123° (1).

3:9432 (1) Sherrill, *J. Am. Chem. Soc.* **52**, 1985–1988 (1930).

$\tilde{C}$ on attempted distillation gave (1) almost quantitative yields of 2,4-dimethylpentadiene-1,3 [Beil. I-257, I_1-(121), I_2-(235)], b.p. 92–93° (1).
[For reactn. of $\tilde{C}$ with phenol + K_2CO_3 in acetone see (1).]

3:9418 (1) Hurd, Cohen, *J. Am. Chem. Soc.* **53**, 1920–1922 (1931).

3:9420 1,2-DICHLOROHEPTANE $C_7H_{14}Cl_2$ **Beil. S.N. 10**

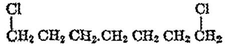


B.P. 68–72° at 7 mm. (1) **D_4^{20} = 1.064 (1) n_D^{20} = 1.4490 (1)**

[For prepn. of $\tilde{C}$ from heptene-1 (1:8324) with Cl_2 in CCl_4 at −15° (13% yield (1)) or with $SOCl_2$ (30–40% yield (1)) see (1).]
$\tilde{C}$ passed over soda-lime at 420° (3% yield) or htd to 250° with powdered KOH in mineral oil (33% yield) loses 2 HCl giving (1) *n*-amylacetylene (1·8085) accompanied by other prods

3:9420 (1) Bachmann, Hill, *J. Am. Chem. Soc.* **56**, 2730–2731 (1934).

3:9422 1,7-DICHLOROHEPTANE $C_7H_{14}Cl_2$ **Beil. I-154**
(Heptamethylene dichloride) I_1—
I_2—



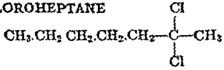
B.P. 120° at 28 mm. (1)

[For prepn. of $\tilde{C}$ (60% yield (1)) from *N,N′-bis*-benzoylheptamethylenediamine [Beil. IX-264] via conversion with PCl_5 to the corresp. *bis*-imidechloride and distillation of the latter see (1); for formn of $\tilde{C}$ (together with other prods.) from heptamethylenediamine [Beil. IV-271] + NOCl see (2).]

Ⓓ **1,7-Diphenoxyheptane** (heptanediol-1,7 *bis*-phenyl ether) [Beil. VI-148]: colorless cyrst. from hot alc., m.p. 53° (1), 54.5–55° (2). [From $\tilde{C}$ on htg. with excess $NaOC_6H_5$ in alc. (1) (2).]

3:9422 (1) von Braun, Müller, *Ber.* **38**, 2347 (1905) (2) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 606–632 (1898); *Cent.* 1898, I 26.

3:9424 2,2-DICHLOROHEPTANE $C_7H_{14}Cl_2$ **Beil. S.N. 10**

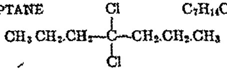


B.P. 77° at 25 mm. (1)

[For prepn. of $\tilde{C}$ from heptanone-2 (*n-amyl methyl ketone*) (1:5460) with PCl_5 (23% yield accompanied by 40% yield of 2-chloroheptene-1 (3:7988)) see (1).]

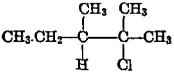
3:9424 (1) Bachmann, Hill, *J. Am. Chem. Soc.* **56**, 2730 (1934).

3:9426 4,4-DICHLOROHEPTANE $C_7H_{14}Cl_2$ **Beil. I-154**
I_1—
I_2-(117)



B.P. 86° at 27 mm. (1) **D_4^{17} = 1.008 (1) n_D^{17} = 1.448 (1) (2)**
60.5° at 11 mm. (2) **1.006 (2)**

3:9442 ***d,l*-2-CHLORO-2,3-DIMETHYLPENTANE** $C_7H_{15}Cl$ **Beil. S.N. 10**
(*sec.*-Butyl-dimethyl-carbinyl chloride)

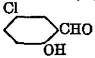


B.P. 38–39° at 20 mm. (1) n_D^{20} **= 1.4264 (1)**

C̄ has been obtd. (1) only as a by-product (10% yield) from the reactn. of 2,3-dimethylpentanol-2 with $AlCl_3$ and C_6H_6; the structure assigned above should be accepted with reserve.

3:9442 (1) Huston, Fox, Binder, *J. Org. Chem.* **3**, 253 (1939).

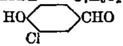
—— **5-CHLORO-2-HYDROXYBENZALDEHYDE** $C_7H_5O_2Cl$ **Beil. VIII-53** **$VIII_1$—**



B.P. 105° at 12 mm. **M.P. 100°**

See 3:2800. *Division A: Solids.*

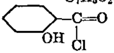
—— **3-CHLORO-4-HYDROXYBENZALDEHYDE** $C_7H_5O_2Cl$ **Beil. VIII-81** **$VIII_1$—**



B.P. 149–150° at 14 mm. **M.P. 139° cor.**

See 3:4065. *Division A: Solids.*

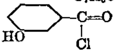
—— **2-HYDROXYBENZOYL CHLORIDE** $C_7H_5O_2Cl$ **Beil. X —** **X_1-(43)**



B.P. 92° at 15 mm. **M.P. 19°** D_-^{20} **= 1.3112** n_-^{20} **= 1.5812**

See 3:0085. *Division A: Solids.*

3:9446 **3-HYDROXYBENZOYL CHLORIDE** $C_7H_5O_2Cl$ **Beil. X —** **X_1-(66)**



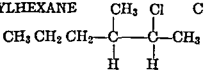
B.P. 110–113° at 0.5 mm. (1)

Pale yel. oil, not solidifying at −15° (2). — C̄ has odor and lachrymatory props. similar to benzoyl chloride; on stdg. even in s.t. turns brown and decomposes (1).

[For prepn. of C̄ from Na or K salts of *m*-hydroxybenxoic acid (1:0825) with $SOCl_2$ (2) or with $COCl_2$ in toluene (3) see indic. refs.]

C̄ with MeOH yields (1) methyl *m*-hydroxybenzoate (1:1468), m.p. 70°, b.p. 178° at 17 mm. (1); C̄ with EtOH yields (1) ethyl *m*-hydroxybenzoate (1:1471), m.p. 73.8°, b.p. 180° at 17 mm. (1); C̄ with dry NH_3 gas in $CHCl_3$ yields (1) *m*-hydroxybenzamide, lfts.

3:9434 2-CHLORO-3-METHYLHEXANE $C_7H_{15}Cl$ Beil. I —
I_1-(58)
I_2—

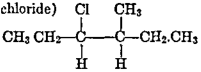


B.P. 53–58° at 36 mm. (1)

[For prepn. of C̄ (80% yield (1)) from 3-methylhexanol-2 [Beil. I_1-(206), I_2-(445)] with PCl_5 see (1).]

3:9434 (1) Bjelouss, *Ber.* **45**, 627–628 (1912).

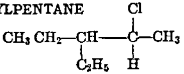
3:9436 4-CHLORO-3-METHYLHEXANE $C_7H_{15}Cl$ Beil. S.N. 10
(*sec.*-Butyl-ethyl-carbinyl chloride)



Only a levorotatory isomer of C̄ has been reported; this resulted from treatment (1) of levorotatory 3-methylhexanol-4 (1) with $SOCl_2$ in pet. ether; b.p 37° at 15 mm. (1).

3:9436 (1) Duveen, Kenyon, *Bull. soc. chim.* (5) **5**, 1120–1126 (1938).

3:9438 2-CHLORO-3-ETHYLPENTANE $C_7H_{15}Cl$ Beil. I —
I_1—
I_2-(120)

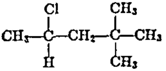


B.P. 62–62.5° cor. at 50 mm. (1) D^{25}_{25} = **0.8911 (1)** n^{25}_D = **1.4295 (1)**
n^{20}_D = **1.4318 (1)**

[For prepn. of C̄ from 3-ethylpentanol-2 [Beil. I 416, I_1-(207), I_2-(445)] (1) with conc. HCl + $ZnCl_2$ at room temp. in 35% yield see (1).]

3:9438 (1) Lucas, *J. Am. Chem. Soc.* **51**, 252 (1929).

3:9440 *d,l*-4-CHLORO-2,2-DIMETHYLPENTANE $C_7H_{15}Cl$ Beil. S.N. 10
(Methyl-neopentyl-carbinyl chloride)



B.P. 93° at 250 mm. (1) D^{20}_4 = **0.855 (1)** n^{20}_D = **1.4180 (1)**
63–65° at 85 mm. (2) **1.4183 (2)**

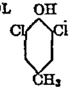
[For prepn. of C̄ from 2,2-dimethylpentanol-4 (methyl-neopentyl-carbinol) satd. with dry HCl and stood 8 weeks (90% yield (1)) or treated with dry HCl under press. for 22 weeks (2) see indic. refs.]

C̄ with Mg in dry ether gives RMgCl; this on oxidn. with O_2 yields (1) 2,2-dimethylpentanol-4, b.p. 136–136.5° at 730 mm. (2), n^{20}_D = 1.4183 (2) (*N*-(α-naphthyl)carbamate, m.p. 84° (1)).

C̄ converted to RMgCl, treated with CO_2, gives (50% yield (2)) methyl-neopentyl-acetic acid, b.p. 109° at 14 mm., n^{20}_D = 1.4233 (2) (amide, m.p. 123° (2); anilide, m.p. 117.5° (2)).

3:9440 (1) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2267 (1938). (2) Whitmore, Noll, Heyd, Surmatis, *J. Am. Chem. Soc.* **63**, 2028 (1941).

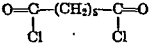
—— 2,6-DICHLORO-4-METHYLPHENOL $C_7H_6OCl_2$ Beil. VI - 403
VI$_1$-(204)
VI$_2$—



B.P. 138–139° at 28 mm. M.P. 38–39°

See 3:0400. *Division A: Solids.*

3:9450 PIMELYL (DI)CHLORIDE $C_7H_{10}O_2Cl_2$ Beil. II - 671
II$_1$—
II$_2$—

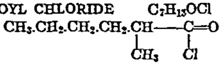


B.P. 137° at 15 mm. (1)

[For prepn. of C̄ from pimelic acid (1:0456) with excess $SOCl_2$ (1) (2) see indic. refs.]
[C̄ with 1 mole MeOH should give 6-carbomethoxyhexanoyl chloride-1, b.p. 135–136° at 17 mm. (3), usually prepd. (3) from methyl hydrogen pimelate + $SOCl_2$.]
C̄ + $AlCl_3$ + C_6H_6 yields (2) 1,5-diphenylpentanedione-1,5.
C̄ on hydrolysis yields pimelic acid (1:0456) (for the dianilide, di-*p*-toluidide, and other derivs. corresp. to C̄ see 1:0456).

3:9450 (1) Blaise, Koehler, *Bull. soc. chim.* (4) 5, 687 (1909). (2) Skraup, Guggenheimer, *Ber.* 58, 2498 (1925). (3) Morgan, Walton, *J. Chem. Soc.* 1935, 291.

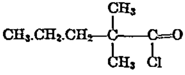
3:9452 *d,l*-α-METHYL-*n*-CAPROYL CHLORIDE $C_7H_{13}OCl$ Beil. II - 342
(*n*-Butyl-methyl-acetyl chloride) II$_1$—
II$_2$-(296)



Physical constants for C̄ appear to be as yet unrecorded. [The dextrorotatory stereoisomer of C̄, b.p. 45–48° at 9 mm. (1) (amide, m.p. 66° (1)), has been obtd. from the dextrorotatory acid with $SOCl_2$ (1).]
[For prepn. of C̄ from *n*-butyl-methyl-acetic acid (1:1134) with PCl_3 (2) or with $SOCl_2$ (3) see indic. refs.]
C̄ on hydrolysis yields 2-methylhexanoic acid-1 (*n*-butyl-methyl-acetic acid) (1:1134) (for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see 1:1134).

3:9452 (1) Levene, Mikeska, *J. Biol. Chem.* 84, 581–582 (1929). (2) Rasetti, *Bull. soc. chim.* (3) 33, 690 (1905). (3) Reichstein, Trivelli, *Helv. Chim. Acta* 15, 258–259 (1932).

3:9456 α,α-DIMETHYL-*n*-VALERYL CHLORIDE $C_7H_{13}OCl$ Beil. S.N. 162
(Dimethyl-*n*-propyl-acetyl chloride)



B.P. 45° at 10 mm. (1)

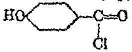
[For prepn. of C̄ from α,α-dimethyl-*n*-valeric acid [Beil. II-345] see (1).]
C̄ on hydrolysis yields α,α-dimethyl-*n*-valeric acid (see above), b.p. 199–200°, 101–102° at 11 mm. (2), 98–99° at 9 mm. (1).

Ⓓ Dimethyl-*n*-propyl-acet-amide: m.p. 95–96° (1) (2).

from hot aq., m.p. 167° (1); C̄ with ... XII-502, XII₁-(269)], ndls. fro[illegible] ...155° (1) (5), C̄ with *p*-toluidine in $CHCl_3$ yields ([illegible] ...benzo-*p*-toluidide, ndls. from dil. alc., m.p. 163° (1).

3:9446 (1) Anschütz, Krone, *Ann.* **442**, 41–42 (1925). (2) Kopetschni, Karczag, Ger. 262,783, July 25, 1913; *Cent.* **1913**, II 728. (3) Kopetschni, Karczag, Ger. 266,351, Oct. 21, 1913; *Cent.* **1913**, II 1715. (4) Klemenc, *Ber.* **49**, 1373 (1916). (5) Kupferberg, *J. prakt. Chem.* (2) **16**, 445 (1877).

3:9447 4-HYDROXYBENZOYL CHLORIDE $C_7H_5O_2Cl$ Beil. X — X_1-(77)



The precise physical props of C̄ have never been reported; it appears to be a yellow oil still liquid at −15° (1) which cannot be distilled with decompn. even in high vac. (2); C̄ has odor and lachrymatory character of benzoyl chloride (2)

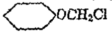
[For prepn. of C̄ from Na or K [illegible] ...nzoic acid (1:0840) with $SOCl_2$ (1) (4) or with [illegible] ... from *p*-hydroxybenzoic acid (1:0840) with 4 [illegible] ..., or $SbCl_5$ see (5).]

C̄ wi[illegible] ... yields methyl *p*-hydroxybenzoate (1:1549), m.p. 131°; C̄ with EtOH yields (2) ethyl *p*-hydroxybenzoate (1:1534), m.p. 116°, 112.5° (2); C̄ with dry NH_3 gas in $CHCl_3$ yields *p*-hydroxybenzamide, ndls. with 1 H_2O from aq., m.p. 162° (2); C̄ with aniline in $CHCl_3$ yields *p*-hydroxybenzanilide [Beil. XII-502, XII₁-(269)], lfts. from hot aq., m.p. 196–197° (2); C̄ with *p*-toluidine in $CHCl_3$ yields *p*-hydroxybenzo-*p*-toluidide, ndls. from alc., m.p. 203–204° (2).

3:9447 (1) Kopetschni, Karczag, Ger. 262,883, July 25, 1913, *Cent.* **1913**, II 728. (2) Anschütz, Zerbe, *Ann.* **442**, 38 (1925). (3) Kopetschni, Karczag, Ger. 266,351, Oct. 21, 1913, *Cent.* **1913**, II 1715. (4) Kopetschni, Karczag, *Ber.* **47**, 237 (1914). (5) Kissling (to I.G.), Ger. 701,953, Jan. 2, 1940; *C.A.* **36**, 99 (1942).

3:9448 PHENOXYMETHYL CHLORIDE C_7H_7OCl Beil. S.N. 514

(Chloromethyl phenyl ether;
α-chloroanisole;
ω-chloroanisole)



Authentic physical constants for this compound are unreported.

[For attempts to prepare C̄ from methylene (di)chloride (3:5020) (1) or from chloromethyl acetate (3:5356) (2) by reaction with sodium phenolate, from formaldehyde diphenylacetal (diphenoxymethane) [Beil. VI-150] by partial cleavage to phenoxymethyl alcohol followed by conversion to C̄ (1), or from anisole (1:7445) by chlorination (3) see indic refs.]

[For claim on use of C̄ in refining of mineral oils see (4).]

3:9448 (1) Bentley, Haworth, Perkin, *J. Chem. Soc.* **69**, 166–167 (1896). (2) Kirner, *J. Am. Chem. Soc.* **48**, 2747–2748 (1926). (3) Weygand, Vogel, *J. prakt. Chem.* (2) **155**, 342–346 (1940). (4) Clarke, Towne (to Texas Co.), U.S. 2,075,269, March 30, 1937; *Cent.* **1937**, II 330; *C.A.* **31**, 3686 (1937).

3:9470 ISOBUTYL *d,l*-α-CHLOROPROPIONATE $C_7H_{13}O_2Cl$ Beil. S.N. 162

$$\begin{array}{c} H \\ | \\ (CH_3)_2CH.CH_2.O.CO.C.CH_3 \\ | \\ Cl \end{array}$$

B.P. — $D_4^{20} = 1.0175$ (1) $n_D^{20} = 1.4230$ (1)

3:9470 (1) Schjanberg, *Z. physik. Chem.* A-172, 230 (1935).

3:9474 *n*-BUTYL β-CHLOROPROPIONATE $C_7H_{13}O_2Cl$ Beil. II —
n-$C_4H_9O.CO.CH_2.CH_2Cl$ II_1—
II_2-(227)

B.P. 104° at 22 mm. (1) $D_4^{20} = 1.0394$ (2) $n_D^{20} = 1.4321$ (2)
97° at 15 mm. (1) $D_4^{15} = 1.0708$ (1) $n_D^{9} = 1.4385$ (1)

[For prepn. from *n*-butyl alc. (1:6180) + β-chloropropionic ac. (3:0460) see (1).]

$\bar{C}$ htd. at 200° with diethylaniline loses HCl and gives (90–100% yield (1)) in distillate *n*-butyl acrylate, b.p. 138–140° at 756 mm. (1).

3:9474 (1) Moureu, Murat, Tampier, *Ann. chim.* (9) 15, 246, 251 (1921). (2) Schjanberg, *Z. physik. Chem.* A-172, 231 (1935).

3:9480 *n*-AMYL α-CHLOROETHYL ETHER $C_7H_{15}OCl$ Beil. S.N. 78
(α-Chloroethyl *n*-amyl ether)

$$\begin{array}{c} H\phantom{.O.n\text{-}C_5H_{11}} \\ |\phantom{.O.n\text{-}C_5H_{11}} \\ CH_3.C.O.n\text{-}C_5H_{11} \\ |\phantom{.O.n\text{-}C_5H_{11}} \\ Cl\phantom{.O.n\text{-}C_5H_{11}} \end{array}$$

B.P. 63.3–66.3° cor. at 8 mm. (1) $D_4^{20} = 0.9200$ (1) $n_D^{20} = 1.4218$ (1)

[For prepn. (99% yield (1)) from paraldehyde (1:0170) + *n*-amyl alc. (1:6205) + dry HCl see (1).]

$\bar{C}$ on stdg. polymerizes to dark tarry residue (1).

$\bar{C}$ on shaking with aq. yields acetaldehyde (1:0100), *n*-amyl alc. (1:6205), + HCl.

3:9480 (1) Henze, Murchison, *J. Am. Chem. Soc.* 53, 4077–4079 (1931).

3:9490 β-CHLOROPROPIONALDEHYDE DIETHYLACETAL Beil. I - 632
$ClCH_2.CH_2\,CH(OC_2H_5)_2$ $C_7H_{15}O_2Cl$ I_1-(335)
I_2-(690)

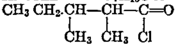
B.P. 84° at 25 mm. (1) $D_4^{22.3} = 0.9845$ (2) $n_D^{22.3} = 1.4203$ (2)
74° at 20 mm. (2) (10) $D_4^{18.7} = 0.9951$ (2) $n_D^{18.1} = 1.4206$ (2)
56–66° at 8 mm. (3)
47–50° at 3–4 mm. (4)

Oil, insol. in aq. but sol. in org. solvents. — $\bar{C}$ may be preserved only if completely free from acid (11) and should be kept over moist K_2CO_3 (3). — $\bar{C}$ on htg. dec. at abt. 145° yielding (1) HCl and acrolein (1:0115).

[For prepn. from acrolein (1:0115) in abs. alc. at 0° with HCl gas (34% yield (5)) (6) (7) (11) (12) in the presence of $CaCl_2$ (90% yield (8), 56% yield (8)) see indic. refs.; for prepn. from α,γ-dichloro-*n*-propyl ethyl ether (9) by reactn. in the cold with EtOH (83% yield (9)) (1) or with NaOEt (1) see indic. refs.]

3:9456 (1) Locquin, Leers, *Compt. rend.* **178**, 2097 (1924). (2) Haller, Bauer, *Compt. rend.* **148**, 129 (1909).

3:9458 α,β-DIMETHYL-*n*-VALERYL CHLORIDE $C_7H_{13}OCl$ **Beil. S.N. 162**
(*sec.*-Butyl-methyl-acetyl chloride)



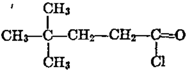
B.P. 110–113° at 193 mm. (1)

[For prepn. of C̄ from α,β-dimethyl-*n*-valeric acid (1) see (1).]
C̄ on hydrolysis yields α,β-dimethyl-*n*-valeric acid, b.p 210.5–210.8° at 750 mm. (1), $D_{18}^{18} = 0.9316$ (methyl ester, b.p. 155–158° at 743 mm. (1)).

Ⓓ α,β-Dimethyl-*n*-valeramide: m p. 101–103° (1)
Ⓓ α,β-Dimethyl-*n*-valeranilide: m.p. 71–72° (1)
Ⓓ α,β-Dimethyl-*n*-valero-*p*-bromoanilide: m.p. 115–117° (1).

3:9458 (1) Chichibabin, Katznelson, *Bull. acad. sci. U.R S S*, *Classe sci. math. nat.* **1933**, 267–271; *Cent.* **1933**, II 3409; *C.A.* **27**, 3698 (1933).

3:9460 γ,γ-DIMETHYL-*n*-VALERYL CHLORIDE $C_7H_{13}OCl$ **Beil. S.N. 162**
(Neopentylacetyl chloride)

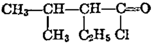


B.P. 94° at 100 mm. (1) $n_D^{20} = 1.4294$ **(1)**

[For prepn. of C̄ from neopentylacetic acid (1) with $SOCl_2$ see (1).]
[C̄ with a large excess of *ter*-BuMgCl (4 moles) gives (1) 67% yield 2,2,6,6-tetramethylheptanol-3, m.p. 58–59° (1) (3,5-dinitrobenzoate, m.p. 99.5° (1); *N*-(α-naphthyl)carbamate, m p. 92° (1)), and 13 5% 2,2-dimethylpentanol-5, b.p. 160° at 728 mm (1), 158° at 737 mm. (2), 96° at 62 mm. (2), $D_4^{20} = 0\ 815$ (2), $n_D^{20} = 1.4202$ (2) (*N*-(α-naphthyl)carbamate, m.p. 80.5–81° (2)).]
C̄ on hydrolysis presumably yields neopentylacetic acid, b.p. 159° at 150 mm. (1), $n_D^{20} = 1.4215$ (1).

3:9460 (1) Whitmore, Whitaker, Mosher, Breivik, Wheeler, Miner, Sutherland, Wagner, Clapper, Lewis, Lux, Popkin, *J. Am. Chem. Soc.* **63**, 647 (1941). (2) Whitmore, Homeyer, *J. Am. Chem. Soc.* **55**, 4558 (1933).

3:9462 α-ETHYL-β-METHYL-*n*-BUTYRYL CHLORIDE $C_7H_{13}OCl$ **Beil. S.N. 162**
(α-Ethyl-isovaleryl chloride; ethyl-isopropyl-acetyl chloride)



B.P. 63–65° at 12 mm. (1)

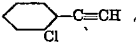
[For prepn. of C̄ from ethyl-isopropyl-acetic acid [Beil. II-345, II_1-(147)] see (1).]
C̄ on hydrolysis yields α-ethyl-isovaleric acid (see above), b.p. 202–203° (1), 202–204° (2).

Ⓓ Ethyl-isopropyl-acet-amide: ndls. from aq., m.p. 136° cor. (3), 134–135.5° (2), 134° (2). [From C̄ + NH_3 at 180° (2).]
Ⓓ Ethyl-isopropyl-acet-anilide: ndls. from lgr., m p. 114–115° (1).
Ⓓ Ethyl-isopropyl-acet-*p*-toluidide: ndls from lt. pet. m p. 122 5–123° (2).

3:9462 (1) Nenitzescu, Chicos, *Ber.* **68**, 1587 (1935). (2) Crossley, Le Sueur, *J. Chem. Soc.* **77**, 94 (1900). (3) Fischer, Rohde, Brauns, *Ann.* **402**, 375–376 (1914).

[illegible] (2) Nef, *Ann.* **308**, 316–323 (1898). (3) Cleve- [illegible] 939). (4) Ott, Bossaller, *Ber.* **76**, 89–90 (1943); *Compt. rend.* **190**, 753–755 (1930). (6) Truchet, *Ann. chim.* (10) **16**, 320–327, 335–337, 340–358 (1931). (7) Murray, *J. Am. Chem. Soc.* **60**, 2663 (1938). (8) Wilson, Wenzke, *J. Am. Chem. Soc.* **56**, 2026 (1934). (9) Gilman, Fothergill, *J. Am. Chem. Soc.* **51**, 3506 (1929).

3:9497 *o*-CHLOROPHENYLACETYLENE C_8H_5Cl Beil. S.N. 474



B.P. 71° at 18 mm. (1) (2) **D_4^{25} = 1.1249 (2) n_D^{25} = 1.5690 (2)**

[For prepn. of C̄ from *o*-chlorophenylpropiolic acid (3:3956) by elimination of CO_2 with $NaHCO_3 + CuCl_2$ (66% yield (1)) or $Cu(OAc)_2$ (yield not stated (2)) see indic. refs.]

[For study of dipole moment see (3).]

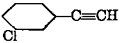
C̄ with PCl_5 (3 wt. pts.) in C_6H_6 stood 24 hrs. then poured into aq gives (54% yield (1)) α-chloro-α-(*o*-chlorophenyl)ethylene-β-phosphinic acid ($C_8H_7O_3Cl_2P$), lfts. from dil. HCl, m.p. 187° (1). — [This prod. with 5% aq. KOH boiled for 6 hrs. loses HCl, giving (1) upon acidification *o*-chlorophenylacetylenephosphinic acid ($C_8H_6O_3ClP$), lfts. from C_6H_6/AcOH, m.p. 134° (1).]

[C̄ with I_2 in liq. NH_3 at −34° readily gives (95% yield (4)) *o*-chlorophenyl-iodo-acetylene, cryst. from MeOH, m.p. 37.7–38.0° (4).]

Ⓓ **Di-(*o*-chlorophenylethynyl)mercury:** m.p. 213–214° (2). [From C̄ in alc. with alk. K_2HgI_4 according to (5); note, however, that m.p. of this prod. is only slightly lower than that (221–222°) of the corresp. prod. from *p*-chlorophenylacetylene (3:0590).]

3:9497 (1) Bergmann, Bondi, *Ber.* **66**, 282–283 (1933). (2) Otto, *J. Am. Chem. Soc.* **56**, 1393–1394 (1934). (3) Otto, Wenzke, *J. Am. Chem. Soc.* **56**, 1314–1315 (1934). (4) Vaughn, Nieuwland, *J. Am. Chem. Soc.* **56**, 1207–1209 (1934). (5) Johnson, McEwen, *J. Am. Chem. Soc.* **48**, 471 (1926).

3:9500 *m*-CHLOROPHENYLACETYLENE C_8H_5Cl Beil. S.N. 474



B.P. 64–65° at 12 mm. (1)

[*See also o-chlorophenylacetylene* (3:9497).]

[For prepn. of C̄ from *m*-chlorophenylpropiolic acid (3:4102) by elimination of CO_2 with $Cu(OAc)_2$ (yield not stated) see (1); for formn. of C̄ from *m*-chlorocumene by pyrolysis see (5).]

[For study of dipole moment see (2).]

[C̄ with I_2 in liq. NH_3 at −34° readily gives (91% yield (3)) *m*-chlorophenyl-iodo-acetylene, m.p. 11.1°, D_4^{25} = 1.818, n_D^{25} = 1.6638 (3).]

Ⓓ **Di-(*m*-chlorophenylethynyl)mercury:** m.p. 138–139° (2), 138.0–138.5° (3). [From C̄ in alc. with alk. K_2HgI_4 according to (4).]

3:9500 (1) Otto, *J. Am. Chem. Soc.* **56**, 1393–1394 (1934). (2) Otto, Wenzke, *J. Am. Chem. Soc.* **56**, 1314–1315 (1934). (3) Vaughn, Nieuwland, *J. Am. Chem. Soc.* **56**, 1207–1209 (1934). (4) Johnson, McEwen, *J. Am. Chem. Soc.* **48**, 471 (1926). (5) Dreisbach (to Dow Chem. Co), U.S. 2,110,830, March 8, 1938; *Cent.* **1938**, I 4110; *C.A.* **32**, 3426 (1938).

C̄ readily hydrolyzes in the presence of dil. acid yielding β-chloropropionaldehyde (3:5576) q.v. and EtOH (1:6130) q.v.

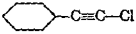
C̄ on refluxing with 2 moles aq. soon undergoes spontaneous reactn., the initial two layers becoming miscible, and after rapid cooling and shaking with conc. $KHSO_3$ or $NaHSO_3$ soln. gives (2) upon addn. of alcohol a ppt. of the corresp. bisulfite cpd. of β-chloropropionaldehyde (3:5576).

[C̄ shaken with a large excess (6 moles) of powdered KOH, then htd at 210–220°, gives (yields: 75% (13), 70% (8)) (10) (3) (12) acrolein diethylacetal (1:0169) q.v., b p. 123°. — C̄ on shaking with dil. aq. NaOH at 115° yields (11) β-hydroxypropionaldehyde diethylacetal [Beil. I-820, I_1-(418)].]

[For reactn. of C̄ with aniline (14) (15), with hydrazine hydrate (16), with alcoholates or phenolates (17), with diethyl sodiomalonate (18), with $MeNH_2$ (19), or with sodium methyl mercaptide (20) see indic. refs.]

3:9490 (1) Brabant, *Z. physiol. Chem.* **86**, 208–209 (1913). (2) Crawford, Kenyon, *J. Chem. Soc.* **1927**, 399. (3) Witzemann, *J. Am Chem. Soc* **36**, 1909–1912 (1914). (4) Hartung, Adkins, *J. Am. Chem. Soc.* **49**, 2521 (1927). (5) Witzemann, Evans, Hass, Schroeder, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 137–138 (1943). (6) Neuberg, Wendisch, *Biochem Z.* **166**, 480 (1925). (7) Evans, Hass, *J. Am. Chem. Soc* **48**, 2705–2706 (1926) (8) Reeves, *J. Chem. Soc.* **1927**, 2481. (9) Dulière, *Bull. soc. chim* (4) **33**, 1651–1652 (1923) (10) Wohl, *Ber* **31**, 1797–1798 (1898). (11) Wohl, Emmerich, *Ber.* **33**, 2761 (1900) (12) Spoehr, Young, *Carnegie Inst Wash. Yearbook* **25**, 175–177 (1925/6), *Expt Sta Record*, **57**, 817, *C A.* **22**, 2368 (1928). (13) Witzemann, Evans, Hass, Schroeder, *Org Syntheses*, *Coll. Vol. 2 (1st ed), 17–18 (1943)* (14) Barr, *J. Am. Chem. Soc* **52**, 2422–2425 (1930) (15) Rath, *Ber* **57**, 717 (1924). (16) Wohl, *Ber.* **64**, 1384 (1931). (17) Schorigin, Korschak, *Ber* **68**, 841–844 (1935) (18) Ellinger, *Ber* **38**, 2886 (1905). (19) Wohl, Johnson, *Ber.* **40**, 4714 (1907). (20) Barger, Coyne, *Biochem. J* **22**, 1420 (1928).

3:9494 α-CHLORO-β-PHENYLACETYLENE C_8H_5Cl Beil. V-513
(Chloroethynylbenzene, phenylethynyl chloride; ω-chlorophenylacetylene) V_1— V_2—



B.P. 74°	at 15 mm. (1)	$D^{18}_{-} = 1.126$ (5) (6) $n^{18}_{D} = 1.576$ (5) (6)
74°	at 14 mm. (2)	$n^{14.9}_{D} = 1.5798$ (6)
73°	at 16 mm. (3)	
72°	at 15 mm. (4)	
71.5°–72°	at 15 mm. (5)	
71°	at 16 mm. (6)	

Colorless mobile liq. with strong and characteristic odor. — Polymerizes rapidly on stdg. with sepn. of crystals (never identified) (7).

[For prepn. of C̄ from sodium deriv. of phenylacetylene (1.7425) in dry ether with p-toluenesulfonyl chloride (65% yield (6)) (3) (7) or benzenesulfonyl chloride (yield 54% (6)) (8) see indic. refs.; from phenylethynyl MgBr in dry ether with benzenesulfonyl chloride (yields: 35% (6), 13 7% (9)) or p-toluenesulfonyl chloride (33% yield (6)) see indic. refs.; from dichloroacetylene (3.5010) with C_6H_5MgX (70% yield) see (4); from sodium or silver salts of phenylacetylene (1:7425) with SO_2Cl_2 in dry ether (small yield) see (2); from ω,ω-dichlorostyrene (α,α-dichloro-β-phenylethylene) [Beil. V-477, V_2-(367)] by elimination of 1 HCl with alc. KOH (1 mole) at 100° for 1 hr. see (2).]

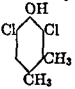
C̄ on protracted boilg. with excess alc. KOH followed by acidification yields (2) (6) phenylacetic acid (1:0665).

[For reactn. of C̄ with diethyl sodiomalonate see (2) (6).]

C̄ does not react with KI in acetone (7).

3:0925 (1) Szenic, Taggesell, *Ber.* 28, 2665–2672 (1895).

3:0935 2,6-DICHLORO-3,4-DIMETHYLPHENOL $C_8H_8OCl_2$ Beil. VI —
(3,5-Dichloro-*o*-4-xylenol) VI_1—
VI_2-(456)



M.P. 52° (1)

Cryst. from lt. pet. — Volatile with steam.

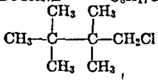
[For prepn. of C̄ from 6-chloro-2-amino-3,4-dimethylphenol (5-chloro-3-amino-*o*-4-xylenol) (1) via diazotization and reaction with Cu_2Cl_2 (yield not stated) see (1); from 2,6-dichloro-3,4-dimethylaniline (3,5-dichloro-*o*-4-xylidine) (2) via diazotization and hydrolysis (yield not stated) see (1).]

The nitration of C̄ has not been reported, and the expected 5-nitro-2,6-dichloro-3,4-dimethylphenol is unknown.

—— **2,6-Dichloro-3,4-dimethylphenyl acetate:** unreported.
Ⓓ **2,6-Dichloro-3,4-dimethylphenyl benzoate:** m.p. 89° (1).

3:0935 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 2532. (2) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 1878.

3:0945 1-CHLORO-2,2,3,3-TETRAMETHYLBUTANE $C_8H_{17}Cl$ Beil. S.N. 10
(Chlorohexamethylethane)



M.P. 52–53° (1) B.P. 80–81° at 40 mm. (1)

Soft waxy solid with characteristic alkyl halide odor; on long stdg. the opaque crystn. structure disappears and C̄ becomes transparent (1).

[For prepn. of C̄ from 2,2,3,3-tetramethylbutane (hexamethylethane) (1:7090) with Cl_2 in CCl_4 soln. in sunlight (33% yield together with other products) see (1).]

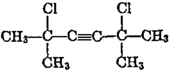
C̄ with Mg + trace of I_2 + a little C_2H_5Br in dry ether gives in 19 hrs. 70% yield corresp. RMgCl (accompanied by 24% 2,2,3,3,6,6,7,7-octamethyloctane, pl. from MeOH, m.p. 74.0–74.5°, from coupling of C̄) (1).

C̄ converted (as above) to RMgCl, treated with wet ether, and poured into dil. H_2SO_4 gives (1) hexamethylethane (1:7090), m.p. 101–102° (1).

C̄ converted to RMgCl (as above) and the ether soln. treated at −5° with CO_2 gives (59% yield (1)) 3,3,4,4-tetramethylpentanoic acid, cryst. from dil. MeOH, m.p. 66–67° (1). [*This acid with $SOCl_2$ in C_6H_6 gives (80% yield (1)) the corresp. acid chloride,* b.p. 87–88° at 20 mm., $D^{20}_{-} = 0.9821$, $n^{20}_{D} = 1.4557$; the latter with dry NH_3 in ether gives (77% yield (1)) the corresp. *amide*, cryst. from $CHCl_3$, m.p. 137–138° (a second cryst. form from MeOH has m.p. 149–150° but after fusion melts 137–138°), or with aniline in ether gives the corresp. *anilide*, cryst. from pet. eth., m.p. 175–176° (1).]

C̄ converted to RMgCl (as above) and the ether soln. treated at −5° with dry O_2 for 4 hrs. gives (53% yield (1)) 2,2,3,3-tetramethylbutanol-1, very volatile solid, m.p. 149–150° [corresp. 3,5-dinitrobenzoate, m.p. 88–90°; *N*-phenylcarbamate, m.p. 65–66° (1)].

3:9504 2,5-DICHLORO-2,5-DIMETHYLHEXYNE-3 $C_8H_{12}Cl_2$ Beil. I —
I_1-(121)
I_2—

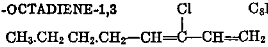


B.P. 62–63° at 15 mm. (1) **M.P. 29° (1)**

[From 2,5-dimethylhexyn-3-diol-2,5 [Beil. I-501, I_1-(263)] with HCl at 0° see (1).]

3:9504 (1) Dupont, *Compt. rend* **152**, 198 (1911).

3:9506 3-CHLORO-OCTADIENE-1,3 $C_8H_{13}Cl$ Beil. S.N. 12



B.P. 64–65° at 18 mm. (1) (3) D_4^{20} = **0.9366 (1)** n_D^{20} = **1.4794 (1)**

[For prepn. of $\bar{C}$ from 1-*n*-butyl-2-vinylacetylene (2) by shaking with conc. HCl contg. $Cu_2Cl_2 + NH_4Cl$ see (1).]

$\bar{C}$ htd. ½ pt. naphthoquinone-1,4 (1:9040) at 100° for 2 hrs., prod. suspended in alc. NaOH and aerated, yields (1) 1-*n*-butyl-2-chloroanthraquinone, yel. ndls. from MeOH, m p. 129–130° (1).

[For polymerization of $\bar{C}$ see (1) (3).]

3:9506 (1) Jacobson, Carothers, *J. Am. Chem. Soc.* **55**, 1624–1627 (1933). (2) Jacobson, Carothers, *J. Am. Chem. Soc.* **55**, 1622–1624 (1933). (3) Carothers, Coffman, U.S. 1,950,441, March 13, 1934; *Cent.* **1934**, II 1037, *C.A.* **28**, 3270 (1934).

3:9510 1-CHLORO-OCTYNE-1 $C_8H_{13}Cl$ Beil. S.N. 12

$CH_3.CH_2\ CH_2\ CH_2\ CH_2\ CH_2—C≡C—Cl$

B.P. 61–62° at 17 mm. (1) D_{-}^{20} = **0.912 (1)** n_D^{20} = **1.445 (1)**

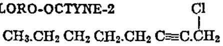
[For prepn. of $\bar{C}$ from octyne-1 (*n*-hexylacetylene) (1.8105) via conversion with $NaNH_2$ to $C_6H_{13}.C≡C—Na$ and reaction in ether with bezenesulfonyl chloride (65% yield (1)) see (1).]

[Refractive indices via Pulfrich instrument: $n_C^{12.7}$ = 1.4447, $n_D^{12.7}$ = 1.4472, $n_F^{12.7}$ = 1.4536, $n_G^{12.7}$ = 1.4589 (1).]

$\bar{C}$ on refluxing for 12 hrs. with alc. KOH gives (70% yield (1)) *n*-caprylic acid (1:1145).

3:9510 (1) Truchet, *Ann. chim.* (10) **16**, 334, 337, 351 (1931).

3:9514 1-CHLORO-OCTYNE-2 $C_8H_{13}Cl$ Beil. S.N. 12

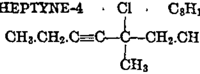


B.P. 80.5–81° at 15 mm. (1)

[For prepn. of $\bar{C}$ from octyn-2-ol-1 [Beil I-456, I_1-(236), I_2-(506)] with PCl_3 see (1).]

3:9514 (1) Toussaint, Wenzke, *J. Am. Chem. Soc.* **57**, 668–669 (1935).

3:9516 3-CHLORO-3-METHYLHEPTYNE-4 $C_8H_{13}Cl$ **Beil. S.N. 12**



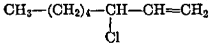
B.P. 55° at 130 mm. (1) D_4^{20} **= 0.9163 (1)** n_D^{20} **= 1.4330 (1)**

[For prepn. of C̄ from 3-methylheptyn-4-ol-3 (1) by saturation with HCl gas (60% yield) see (1).]

[C̄ with MeMgBr gives (66% yield) 3,3-dimethylheptyne-4, b.p. 69° at 100 mm., D_4^{20} = 0.7610, n_D^{20} = 1.4360 (1); C̄ with EtMgBr gives (61% yield) 3-ethyl-3-methyl-heptyne-4, b p. 88° at 100 mm., D_4^{20} = 0.7714, n_D^{20} = 1.4386 (1).]

3:9516 (1) Campbell, Eby, *J. Am. Chem. Soc.* **62**, 1799–1800 (1940).

3:9518 *d,l*-3-CHLORO-OCTENE-1 $C_8H_{15}Cl$ **Beil. S.N. 11**

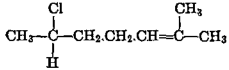


No record of this compound can be found in the literature.

[Note, however, that the levorotatory enantiomorph has been reported (1).]

3:9518 (1) Levene, Rothen, *J. Chem. Phys.* **5**, 982 (1937).

3:9520 6-CHLORO-2-METHYLHEPTENE-2 $C_8H_{15}Cl$ **Beil. I —**
I_1—
I_2-(200)



B.P. 60–61° at 15 mm. (1) D_4^{18} **= 0.8931 (1)** n_D^{18} **= 1.4458 (1)**
59–61° at 15 mm. (2)

Colorless mobile liq., insol. aq., sol. in usual org. solvents.

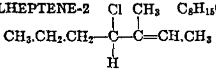
[For prepn. from 2-methylhepten-2-ol-6 [Beil. I-448, I_1-(230), I_2-(490)] with $SOCl_2$ + pyridine (39% yield (1)) see (1) (2).]

C̄ could not be induced to yield an R.MgCl cpd. (2).

C̄ in AcOH treated with O_3 and the soln. subsequently shaken with Zn dust gives (61% yield (1)) γ-chloro-*n*-valeraldehyde, b.p. 70–71° at 16 mm. (1).

3:9520 (1) Helferich, Dommer, *Ber.* **53**, 2008–2009 (1920). (2) Doeuvre, *Bull. soc. chim.* (4) **45**, 359–360 (1929).

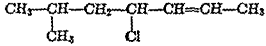
3:9524 *d,l*-4-CHLORO-3-METHYLHEPTENE-2 $C_8H_{15}Cl$ **Beil. I —**
I_1-(94)
I_2—



[For prepn. of C̄ from 3-methylhepten-2-ol-4 (1) with 6 *N* HCl see (1).]

3:9524 (1) Abelmann, *Ber.* **43**, 1581 (1910).

3:9525 4-CHLORO-6-METHYLHEPTENE-2 $C_8H_{15}Cl$ Beil. S.N. 11
(4-Chloro-2-methylheptene-5)

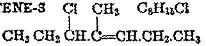


B.P. 57° at 13 mm. (1)

[For prepn. of C̄ from 6-methylhepten-2-ol-4 with HCl see (1).]

3:9525 (1) Knorr (to I.G.), Ger. 553,279, June 24, 1932; *Cent.* **1932**, II 2370; *C.A.* **26**, 4611 (1932).

3:9526 5-CHLORO-4-METHYLHEPTENE-3 $C_8H_{15}Cl$ Beil. I — I_1-(94) I_2-(201)



B.P. 75–78° at 53 mm. (1)

Two geom. stereoisomers of C̄ are possible, but only this one is as yet recorded.

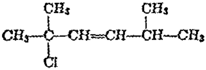
[For prepn. of C̄ from 4-methylhepten-3-ol-5 [Beil. I_1-(201), I_2-(491)] by distn. with conc. HCl (1) (3) or by saturation with dry HCl gas at 0° (2) see indic. refs.]

C̄ is very reactive toward aq; at 15° C̄ is 93% hydrolyzed in 48 hrs., at 45–50° 90% hydrolyzed in 75 min (2)

C̄ on oxidn. with $Na_2Cr_2O_7 + H_2SO_4$ at 45–50° yields (2) 4-methylhepten-3-one-5 [Beil. I_2-(799)], b.p. 170–172° at 735 mm, 96–98° at 70 mm, $D_4^{15} = 0.8773$, $n_D^{15} = 1.4510$ (2,4-dinitrophenylhydrazone, m.p. 147°, semicarbazone, m.p. 167° (2)).

3:9526 (1) Bjelouss, *Ber.* **43**, 2331 (1910). (2) Courtot, Pierron, *Bull soc chim.* (4) **45**, 292 (1929). (3) Knorr (to I.G.), Ger. 553,279, June 24, 1932, *Cent.* **1932**, II 2370.

3:9527 2-CHLORO-2,5-DIMETHYLHEXENE-3 $C_8H_{15}Cl$ Beil. S.N. 11
(Di-isocrotyl hydrochloride)



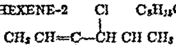
C̄ has never been reported in pure form; note that, in addition to the possibility of existence of two geometrical stereoisomers, C̄ by virtue of allylic rearrangement can yield 4-chloro-2,5-dimethylhexene-2 (3:9529) q.v.

[For prepn. of C̄ (as a mixt. with some or all of these other compds.) from 2,5-dimethylhexadiene-2,4 ("di-isocrotyl") [Beil. I-259, I_1-(122), I_2-(237)] by addn. of dry HCl gas see (1); note that the reaction prod. has b.p. 45–60° at 15 mm., $n_D^{20} = 1.45$ to 1.46, and although stable in the cold decomposes on attempts to effect fractional distn.]

[C̄ with MeMgCl *yields* (1) *mainly* 2,4,5-trimethylhexene-2 [Beil. I_1-(95)], b.p. 128.4° at 760 mm. (1), $D_4^{20} = 0.7403$ (1), $n_D^{20} = 1.4268$ (1), accompanied by some 2,2,5-trimethylhexene-3, b.p. 114° at 760 mm. (1), $n_D^{20} = 1.416$ (1).]

3:9527 (1) Henne, Chanan, Turk, *J. Am. Chem. Soc.* **63**, 3474–3476 (1941).

3:9528 4-CHLORO-3,5-DIMETHYLHEXENE-2 $C_8H_{15}Cl$ Beil. I — I_1-(94) I_2—

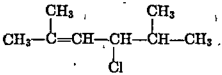


B.P. 58–60° at 21 mm. (1)

[For prepn. of C̄ from 2,4-dimethylhexen-4-ol-3 (1) with 6 N HCl (80% yield) see (1).]

3:9528 (1) Abelmann, *Ber.* **43**, 1581–1582 (1910).

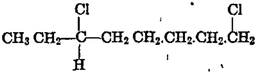
3:9529 4-CHLORO-2,5-DIMETHYLHEXENE-2 $C_8H_{15}Cl$ Beil. S.N. 11



C̄, the allylic rearr. prod. of 2-chloro-2,5-dimethylhexene-3 (3:9527) q.v., has never been reported in pure form (1).

3:9529 (1) Henne, Chanan, Turk, *J. Am. Chem. Soc.* **63**, 3474–3476 (1941).

3:9530 *d,l*-1,6-DICHLORO-OCTANE $C_8H_{16}Cl_2$ Beil. I —
I_1—
I_2-(124)

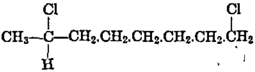


B.P. 105–107° at 16 mm. (1)

[For prepn. of C̄ from N-benzoyl-2-n-propylpiperidine (N-benzoylconiine) [Beil. XX-116] by conversion with PCl_5 to the amide-chloride $C_8H_{16}N.C(Cl)_2.C_6H_5$ followed by rapid distn. of the latter see (1).] [This prod. was originally (1) thought to be 1,5-dichloro-octane [Beil. I-160] but is now regarded (2) as C̄.]

3:9530 (1) von Braun, Schmitz, *Ber.* **39**, 4366 (1906). (2) von Braun, Pohl, *Ber.* **57**, 482–483 (1924).

3:9532 *d,l*-1,7-DICHLORO-OCTANE $C_8H_{16}Cl_2$ Beil. I-160
I_1—
I_2—



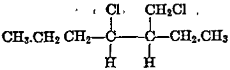
B.P. 132–138° at 20-25 mm. (1)

[For prepn. of C̄ from octamethylenediamine [Beil. IV-271] with NOCl see (1). The prod. is admittedly impure and contains also 8-chloro-octene-2 and 1,8-dichloro-octane (3:8805).]

C̄ on htg. with sodium phenolate yields (1) 1,7-diphenoxyoctane [Beil. VI-148], b.p. 240–250° at 20–25 mm., not volatile with steam.

3:9532 (1) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 620–621 (1898); *Cent.* **1898**, I 26.

3:9534 4-CHLORO-3-(CHLOROMETHYL)-HEPTANE $C_8H_{16}Cl_2$ Beil. S.N. 10

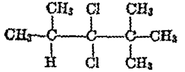


B.P. 50° at 0.2 mm. (1)

[For prepn. of C̄ from 2-ethylhexanediol-1,2 with conc. HCl at 120° see (1).]

3:9534 (1) von Braun, Manz, *Ber.* 67, 1704–1705 (1934).

3:9536 3,3-DICHLORO-2,2,4-TRIMETHYLPENTANE $C_8H_{16}Cl_2$ Beil. I —
(Pentamethylacetone dichloride) I_1-(62)
I_2—

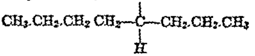


B.P. 122–125° at 19 mm. (1)

[For prepn. of C̄ from 2,2,4-trimethylpentanone-3 (pentamethylacetone) [Beil. I-708, I_1-(364), I_2-(760)] with PCl_5 in s.t. for 60 hrs. at 140° (1) (together with other products) see (1).]

3:9536 (1) Favorskii, Fritzman, *J. Russ. Phys.-Chem. Soc.* **44**, 1353 (1912); *Cent.* **1913**, I 1007; *C.A.* 7, 985 (1913); *J. prakt. Chem.* (2) 88, 654 (1913).

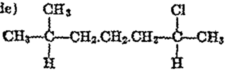
3:9538 *d,l*-4-CHLORO-OCTANE $C_8H_{17}Cl$ **Beil. S.N. 10**
(*n*-Butyl-*n*-propyl-carbinyl chloride)



C̄ as such is as yet unreported; however, the dextrorotatory isomer of C̄ has been obtd. (1) *from the metathesis of levorotatory 4-iodooctane with LiCl in MeOH; b.p. 92° at 50 mm.*

3:9538 (1) Levene, Rothen, Kuna, *J. Biol. Chem.* **120**, 786 (1937).

3:9540 *d,l*-6-CHLORO-2-METHYLHEPTANE $C_8H_{17}Cl$ **Beil. S.N. 10**
(Isohexyl-methyl-carbinyl chloride)



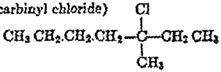
B.P. 74–75° at 35 mm. (1) n_D^{15} = **1.4260 (1)**

[For prepn. of C̄ from 2-methylheptanol-6 [Beil. I-421, I_1-(209), I_2-(453)] with $SOCl_2$ in cold $CHCl_3$ + dimethylaniline, then refluxed 2 hrs., see (1).]

C̄ with activated Mg in dry ether gives with difficulty not over 41% of RMgCl (by carbonation and titration of the resultant acid (1)).

3:9540 (1) Peak, Robinson, *J. Chem. Soc.* **1937**, 1589–1590.

3:9544 3-CHLORO-3-METHYLHEPTANE $C_8H_{17}Cl$ **Beil. S.N. 10**
(*n*-Butyl-ethyl-methyl-carbinyl chloride)

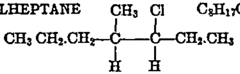


B.P. 64–65° at 27 mm. (1) D_4^{25} = **0.8720 (2)** n_D^{25} = **1.4293 (3)**
55° at 15 mm. (2) D_4^{20} = **0.8764 (2)** n_D^{20} = **1.4317 (3)**
1.4314 (1)
1.4205 (2)

[For prepn. of C̄ from 3-methylheptanol-3 (*n*-butyl-ethyl-methylcarbinol) [Beil. I-421, I_2-(453)] (1) (2) with dry HCl gas at −10° (2) or at 10–15° (92% yield (1)) see indic. refs.]
C̄ with Mg in dry ether as specified (1) gives 70% yield corresp. RMgCl.
C̄ converted as above to RMgCl, treated with formaldehyde gas, gives (31% yield (1)) 2-ethyl-2-methylhexanol-1, b.p. 85.5–86° at 11 mm., $n_D^{20} = 1.4401$ (1).

3:9544 (1) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1560–1562, 1565 (1933). (2) Whitmore, Woodburn, *J. Am. Chem Soc.* **55**, 361–365 (1933). (3) Smart, Quayle, *J. Am. Chem. Soc.* **67**, 21 (1945).

3:9548 3-CHLORO-4-METHYLHEPTANE $C_8H_{17}Cl$ Beil. I —
I_1-(61)
I_2—

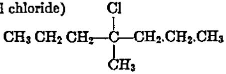


B.P. 83–86° at 79 mm. (1)

[For prepn. of C̄ from 4-methylheptanol-3 with PCl_5 see (1).]

3:9548 (1) Bjelouss, *Ber.* **45**, 628 (1912).

3:9550 *d,l*-4-CHLORO-4-METHYLHEPTANE $C_8H_{17}Cl$ Beil. I —
(Methyl-di-*n*-propyl-carbinyl chloride) I_1-(62)
I_2—

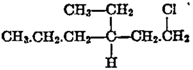


B.P. 50–51° at 12 mm. (1) (3) $D_4^{20} = 0.8690$ **(1)** $n_D^{15} = 1.43098$ **(1)**

[For prepn. of C̄ from 4-methylheptanol-4 (methyl-di-*n*-propyl-carbinol (1)) by saturation with HCl gas see (1).]
[For data on density of C̄ at 15°, 25°, 50°, and 65° and value of parachor at 0°, 25°, 50°, and 75° see (2).]
[C̄ with C_6H_6 + $AlCl_3$ gives (64% yield (1)) 4-methyl-4-phenyl-heptane, b.p. 120–121° at 12 mm., $D_4^{20} = 0.8708$, $n_D^{15} = 1.49326$ (1); for behavior with naphthalene + $AlCl_3$ in CS_2 see (3).]

3:9550 (1) Halse, *J. prakt. Chem.* (2) **89**, 453–454 (1914). (2) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3108 (1939). (3) Petrov, Kurbskii, *J. Gen. Chem.* (*U.S.S.R.*) **14**, 492–494 (1944); *C.A.* **39**, 4600 (1945).

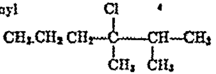
3:9552 *d,l*-1-CHLORO-3-ETHYLHEXANE $C_8H_{17}Cl$ Beil. S.N. 10



C̄ as such is as yet unreported; however, the dextrorotatory isomer of C̄ has been prepared from dextrorotatory 3-ethylhexanol-1 (1) with $SOCl_2$; b.p. 85° at 40 mm., $D_4^{27} = 0.879$, $n_D^{25} = 1.4335$ (1).

3:9552 (1) Levene, Marker, *J. Biol. Chem.* **91**, 699–700 (1931).

3:0554 3-CHLORO-2,3-DIMETHYLHEXANE $C_8H_{17}Cl$ Beil. S.N. 10
(Isopropyl-methyl-*n*-propyl-carbinyl chloride)

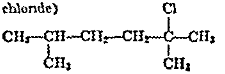


B.P. 41–43° at 12 mm. (1) $D_4^{20} = 0.8860$ (1) $n_D^{25} = 1.4333$ (2)
$n_D^{20} = 1.4353$ (2)
1.4350 (1)

[For prepn. from 2,3-dimethylhexanol-3 {Beil. I₁-(210), I₂-(454)} (2) (1) with dry HCl gas at 0° (81% yield (1)) see (1) (2).]

3:0554 (1) Whitmore, Evers, *J. Am. Chem. Soc.* **55**, 813–814 (1933). (2) Stevens, Greenwood, *J. Am. Chem. Soc.* **65**, 2152–2153 (1943).

3:0556 2-CHLORO-2,5-DIMETHYLHEXANE $C_8H_{17}Cl$ Beil. I —
(Isoamyl-dimethyl-carbinyl chloride) I₁-(62)
I₂—



B.P. 80° at 100 mm. (1) $n_D^{20} = 1.4232$–
44–45° at 14 mm. (2) 1.4240 (1)
$D_4^{15} = 0.8476$ (2) $n_D^{15} = 1.4295$ (2)

[For prepn. of Č from 2,5-dimethylhexanol-2 (isoamyl-dimethyl-carbinol) (2) by saturation with HCl gas (79% yield (2)) see (1) (2); for formn. of Č (together with other prods.) during hydrolysis of 2-nitroso-2,5-dimethylhexane see (1).]

[Č with C_6H_6 + $AlCl_3$ gives 2,5-dimethyl-2-phenylhexane, b.p. 116–117° at 14 mm., $D_4^{15} = 0.8841$, $n_D^{15} = 1.50233$ (2).]

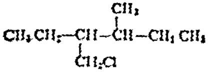
3:0556 (1) Aston, Allman, *J. Am. Chem. Soc.* **60**, 1931 (1938). (2) Halse, *J. prakt. Chem.* (2) **89**, 455 (1914).

3:0558 2-CHLORO-3,4-DIMETHYLHEXANE $C_8H_{17}Cl$ Beil. S.N. 10

No physical constants on this compound are recorded; for its formation, however, as a by-product of the addition of HCl to butene-2 see (1).

3:0558 (1) Coffin, Sutherland, Maass, *Can. J. Research* **2**, 275–278 (1930).

3:0560 4-(CHLOROMETHYL)-3-METHYLHEXANE $C_8H_{17}Cl$ Beil. S.N. 10



150° (42) (40), 149° (41); C̄ with acenaphthene gives (65–68% yield (43)) 5-(phenylacetyl)-acenaphthene (4-acenaphthyl benzyl ketone), m.p. 114° (43); C̄ with bromobenzene (in CS_2) gives (44) 4-bromodesoxybenzoin, m.p. 114–115°, b p. 165° at 3 mm. (44).] — [For *oxidn. of many of these with SeO_2 to corresp. benzils see* (38).]

[C̄ with phenols + $AlCl_3$ (often in nitrobenzene) similarly yields hydroxy-substituted desoxybenzoins: *e g.*, C̄ with phenol as directed gives (60–70% yield (45)) 4-hydroxydesoxybenzoin [Beil. VIII-165], m.p. 142° cor. (45); C̄ with *o*-cresol gives (60–70% yield (46)) 4-hydroxy-3-methyldesoxybenzoin [Beil. VIII-183], m.p. 152° (46); C̄ with salicylic acid (1:0780) gives (47) 4-hydroxy-3-carboxy-desoxybenzoin; for similar reactn. with catechol resorcinol, and hydroquinone (48) or with phloroglucinol (49) see indic. refs.]

[C̄ with phenol ethers + $AlCl_3$ (often in nitrobenzene) similarly yields substituted desoxybenzoins: *e.g.*, C̄ with anisole (1:7445) + $SnCl_4$ (51) or $AlCl_3$ (34) (50) gives 4-methoxydesoxybenzoin [Beil. VIII-166, $VIII_1$-(571)], m.p. 77°; C̄ with methyl *m*-tolyl ether (1:7510) + $SnCl_4$ (not $AlCl_3$) gives (60–70% yield (51)) (50) 4-methoxy-2-methyl-*desoxybenzoin, m.p. 76.5° (51); C̄ with methyl p-tolyl ether (1:7495) + $AlCl_3$ in CS_2* gives (11) 2-methoxy-5-methyldesoxybenzoin, m.p. 75°, b.p. 205–207° at 14 mm. (11).]

C̄ with phenols on htg. gives corresp. esters: *e.g.*, C̄ with phenol at 150° for 8 hrs. (6) (or C̄ with phenol + aq. alk. (52)) yields phenyl phenylacetate [Beil. IX-435], ndls. from lt. pet., m.p. 50° (6), 42° (52); C̄ with *β*-naphthol at 150° for 6 hrs. yields (6) *β*-naphthyl phenylacetate, pl. from lt. pet., m.p. 87° (6); C̄ with *o*-cresol at 90° yields (9) *o*-tolyl phenylacetate, m.p. 44–45° (9); C̄ with *m*-cresol at 90° yields (9) *m*-tolyl phenylacetate, m p. 51–52° (9); C̄ with *p*-cresol at 90° yields (9) *p*-tolyl phenylacetate, m.p. 74–75° (9).

[C̄ with MeZnI (53) in toluene + EtOAc or with Me_2Zn (54) gives (72% yield (53)) benzyl methyl ketone (phenylacetone) (1:5118); C̄ with EtZnI (53) or with Et_2Zn (54) gives (78% yield (53)) benzyl ethyl ketone [Beil. VII-314, VII_1-(167)]]

[C̄ + o-hydroxyacetophenone (1:1746) + NaĀ at 180° for 6 hrs. followed by hydrol. with alc. KOH gives (6) 4-methyl-3-phenylcoumarin, m.p. 153° (6); C̄ with 2-hydroxy-5-methylbenzophenone + NaĀ at 180° gives (80–90% yield (55)) 3,4-diphenyl-6-methylcoumarin, cryst. from AcOH, m.p. 208–209° (55).]

[C̄ with diazomethane in ether gives acc. to cond. (56) (57) (58) (62) either (yield: 84% (56), 83% (62)) *α*-chloro-*γ*-phenylacetone [Beil. VII_1-(162)], m p. 72–73° (56), b.p. 133–135° at 19 mm. (62), $n_D^{20} = 1.5379$ (62), or *α*-diazo-*γ*-phenylacetone (identified by reactn. with *p-nitrobenzoic acid yielding (58) α-(p-nitrobenzoyloxy)-α-phenylacetone,* pl. *from* alc., m.p. 120° (58)); note, however, that work of (56) could not be duplicated by later investigators (58) (62).]

[C̄ with biuret yields (59) N_1-(phenylacetyl)biuret, cryst. from alc., m.p. 199–200° u.c. dec. (59).]

[C̄ with ethyl carbamate (urethane) at 60–70° gives (70% yield (60)) ethyl *N*-(phenylacetyl)carbamate, m.p. 113° (60).]

[C̄ with MeOH yields methyl phenylaretate (1:3771), b.p. 220°; C̄ with EtOH yields *ethyl phenylacetate (1:3872),* b.p. 227.5°.] [For use in prepn. of cellulose esters see (61).]

C̄ on hydrolysis yields phenylacetic acid (1:0665), m.p. 76.5°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see phenylacetic acid (1:0665)

3:9567 (1) Perkin, *J. Chem. Soc.* **69**, 1205 (1896) ... 49, 1428–1429
(1931). (3) Martin, Partington, *J. Chem. Soc*
(1896). (5) Fourneau, Nicolitch, *Bull. soc. chi*
Venkatarman, *J. Chem. Soc.* **1933**, 1461–1462.
(8) Bergs, *Ber.* **67**, 240–241 (1934). (9) Raifo
(1929); *Cent.* **1930**, I 209. (10) Rupe, *Ann.* **369**, 330 (1909).
(11) von Auwers, *Ber.* **53**, 2277, 2282–2283 (1920). (12) Kohlrausch, Pongratz, *Monatsh.* **64**, 382 (1934). (13) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (14) Adams,

Ulich, *J. Am. Chem. Soc.* **42**, 604 (1920). (15) Möller, Strecker, *Ann.* **113**, 68 (1860). (16) Vanino, Thiele, *Ber.* **29**, 1727, Note (1896). (17) Ivanov, Nicolov, *Bull. soc. chim.* (4) **51**, 1333 (1932). (18) Weiss, *Monatsh.* **40**, 391-395 (1919). (19) Metzner, *Ann.* **298**, 375-376 (1897). (20) Allen, Barker, *Org. Syntheses* **12**, 16-18 (1932), Coll. Vol. **2** (1st ed.), 156-158 (1943).

(21) Aeschliman, *J. Chem. Soc.* **1926**, 2909. (22) Meyer, *Monatsh.* **22**, 427-428 (1901). (23) Montonna, *J. Am. Chem. Soc.* **49**, 2114-2116 (1927). (24) Rupe, Fiedler, *J. prakt. Chem.* (2) **84**, 814 (1911). (25) Wedekind, *Ber.* **34**, 2074-2077 (1901). (26) Durrans, *J. Chem. Soc.* **121**, 49 (1922). (27) Wedekind, *Ann.* **378**, 262-268, 275-283 (1910). (28) Rosenmund, Zetsche, *Ber.* **54**, 437 (1921). (29) Fröschl, Danoff, *J. prakt. Chem.* (2) **144**, 223-224 (1936). (30) Grignard, Mingasson, *Compt. rend.* **185**, 1176 (1927).

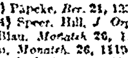
(31) von Braun, Kochendörfer, *Ber.* **56**, 2176 (1923). (32) Sugasawa, Tsuda, *J. Pharm. Soc. Japan* **56**, 103-105 (1936); *Cent.* **1936**, II 3670. (33) Graebe, Bungener, *Ber.* **12**, 1079-1080 (1879). (34) Tiffeneau, Levy, Ditz, *Bull. soc. chim.* (5) **2**, 1873-1874, 1875 (1935). (35) Mann, *Ber.* **14**, 1646 (1881). (36) Kayser, *Ann. chim.* (11) **6**, 187-188 (1936). (37) Wege, *Ber.* **24**, 3540-3542 (1891). (38) Hatt, Pilgrim, Hurran, *J. Chem. Soc.* **1936**, 94-95. (39) Ruggli, Reinert, *Helv. Chim. Acta* **9**, 71-74 (1926). (40) Ferns, Turner, *J. Chem. Soc.* **117**, 1148-1149 (1920).

(41) Delaville, *Compt. rend.* **184**, 463 (1927). (42) Päpcke, *Ber.* **21**, 1339 (1888). (43) Ruggli, Jenney, *Helv. Chim. Acta* **10**, 231-232 (1927). (44) Speer, Hill, *J. Org. Chem.* **2**, 142 (1937). (45) Weidl, *Monatsh.* **26**, 986-987 (1905). (46) Blau, *Monatsh.* **26**, 1151-1153 (1905). (47) Glassner, *Monatsh.* **28**, 282-285 (1907). (48) Finzi, *Monatsh.* **26**, 1119-1138 (1905). (49) K. Rosenmund, M. Rosenmund, *Ber.* **61**, 2610 (1928). (50) Ney, *Ber.* **21**, 2450-2451 (1888).

(51) Hill, Short, *J. Chem. Soc.* **1935**, 1125. (52) Stoermer, Biesenbach, *Ber.* **38**, 1962 (1905). (53) Morgan, Drew, Porter, *Ber.* **58**, 339-341 (1925). (54) Popov, *J. Russ. Phys.-Chem. Soc.* **4**, 214 (1872); *Ber.* **5**, 500-502 (1872). (55) Ziegler, Fries, Sälzer, *Ann.* **448**, 261 (1926). (56) Childens, Nierenstein, *J. Chem. Soc.* **107**, 1492 (1915). (57) Lewis, Nierenstein, Rich, *J. Am. Chem. Soc.* **47**, 1729 (1925). (58) Bradley, Schwarzenbach, *J. Chem. Soc.* **1928**, 2906. (59) Ostrogovich, Tanislau, *Gazz. chim. ital.* **64**, 825-828 (1934); *Cent.* **1935**, I 2820. (60) Basterfield, Woods, Wright, *J. Am. Chem. Soc.* **48**, 2371-2372 (1926).

(61) I.G., Brit. 305,947, April 10, 1929; *Cent.* **1929**, II 112. (62) McPhee, Klingsberg, *J. Am. Chem. Soc.* **66**, 1134-1135 (1944).

3:9570 *dl*-CHLOROMETHYL-PHENYL-CARBINOL C_8H_9OCl Beil. VI —
(β-Hydroxy-β-phenylethyl chloride, VI₁-(236)
α-(chloromethyl)benzyl alcohol, VI₂-(446)
styrene chlorohydrin)



B.P. 128° at 17 mm. (1) n_D^{22} = 1.5538 (2)
118-120° at 14 mm. (2) 1.5520 (2)
112-114° at 10 mm. (3) $D_4^{20.5}$ = 1.1610 (1) $n_D^{20.5}$ = 1.5400 (1)
110-111° at 6 mm. (4)
110-112° at 5 mm. (5) $D_4^{?}$ = 1.225 (1) n_D^{17} = 1.55103 (1)

[For prepn. of C̄ from phenylethylene (styrene) (1:7435) by addition of HOCl generated from $Ca(OCl)_2 + CO_2$ (76% yield (2)), from $NaOCl + CO_2$ (6), from *N*-chlorourea + AcOH (yield: 70% (1), 52% (4)), or from *tert*-butyl hypochlorite (3:7165) in dil. AcOH (60-70% yield (4)) see indic. refs. (note that omission of AcOH in *tert*-BuOCl method leads to formn. by direct addn. (4) of chloromethyl-phenylcarbinyl *tert*-butyl ether, b.p. 67-68° at 1.5 mm., D_4^{15} = 1.0549, n_D^{15} = 1.5102 (4)).]

[For prepn. of C̄ from chloroacetaldehyde (3:7212) with C_6H_5MgBr in ether (71% yield (3)) or from α,β-dichloroethylbenzene (styrene dichloride) (3:6985) with a mild dehydrochlorinating agent such as Na_2CO_3, NaOAc, CaO, or $CaCO_3$ (but not an alkali hydroxide) and water (2) see indic. refs.]

[C̄ with alc. KOH (1) or with an alk. or alk. earth metal oxide or hydroxide as directed (7) (8) loses HCl with ring closure to phenylepoxyethane (styrene oxide) (Beil. XVII-49) (7), b.p. 191-192°, but no phenylacetaldehyde (1:0200) is formed (1) (for use of this

conversion to remove $\bar{C}$ from mixtures with styrene dichloride (3:6685) see (7) (8)). — However, $\bar{C}$ with NaOEt gives (yield not reported (1)) cf. (3) ethyl β-hydroxy-β-phenylethyl ether [Beil. VI-907], b.p. 242–243°.]

[$\bar{C}$ on dehydration by passing over HPO_3 on silica gel at 370–400° and 95–115 mm. press. gives (63% yield (9)) β-chlorostyrene (3:8717).]

[$\bar{C}$ on passing over activated Al_2O_3 at 360–390° and 115–125 mm. press. gives (67% yield (9)) acetophenone (1:5515), but $\bar{C}$ on passing over $CaCO_3$ on silica gel at 325–350° and 105–125 mm. press. gives (51% yield (9)) phenylacetaldehyde (1:0200).]

$\bar{C}$ with pyridine at 120° for 6 hrs. gives in quant. yield (10) the corresp. quaternary pyridinium salt; m.p. 210–212° dec., sol. in aq., MeOH, EtOH, but spar. sol. in other org. solvents.

$\bar{C}$ on oxidn. with $K_2Cr_2O_7/H_2SO_4$/AcOH at low temp. (1) cf. (4) gives (84% yield (4)) ω-chloroacetophenone (phenacyl chloride) (3:1212).

——*Chloromethyl-phenyl-carbinyl acetate: b.p. 101–104° at 3 mm.*, $n_D^{12} = 1.5182$ (4). [From $\bar{C}$ with Ac_2O + pyridine (66% yield (4)).]

—— **Chloromethyl-phenyl-carbinyl benzoate:** unreported.

Ⓓ **Chloromethyl-phenyl-carbinyl *p*-nitrobenzoate:** m.p. 81° (4). [From $\bar{C}$ with *p*-nitrobenzoyl chloride in pyridine (4).]

—— **Chloromethyl-phenyl-carbinyl 3,5-dinitrobenzoate:** unreported.

3:9570 (1) Detoeuf, *Bull. soc. chim.* (4) **31**, 176–177 (1922). (2) Emerson, *J. Am. Chem. Soc.* **67**, 516–518 (1945). (3) Späth, *Monatsh.* **36**, 6–7 (1915). (4) Hanby, Rydon, *J. Chem. Soc.* **1946**, 114–115. (5) I.G., French 735,108, Nov. 3, 1932; *Cent.* **1933**, II 1093; *C.A.* **27**, 1011 (1933). (6) Essex, Ward (to du Pont Co), U.S. 1,594,608, Aug. 3, 1926; *Cent.* **1926**, II 1693; *C.A.* **20**, 3170 (1926). (7) I.G., Brit. 381,459, Oct. 27, 1932; *Cent.* **1933**, I 506; *C.A.* **27**, 3950 (1933). (8) Knorr (to I.G.) Ger. 559,521, Sept. 21, 1932; *Cent.* **1933**, I 1843; *C.A.* **27**, 736 (1933): French 735,000, Oct. 31, 1932; *Cent.* **1933**, I 1843; *C.A.* **27**, 1011 (1933). (9) Emerson, Agnew, *J. Am. Chem. Soc.* **67**, 518–520 (1945). (10) Gautier, *Compt. rend.* **198**, 1430–1431 (1934).

3:9576 SUBERYL (DI)CHLORIDE $C_8H_{12}O_2Cl_2$ Beil. II - 694, II_1-(287), II_2-(596)

$$\underset{\displaystyle Cl}{\overset{}{O{=}\underset{|}{C}}}{-}(CH_2)_6{-}\underset{\displaystyle Cl}{\overset{}{\underset{|}{C}{=}O}}$$

B.P. 162–163°	at 15 mm., sl. dec.	(1)
159–160°	at 12 mm.	(2)
149–150°	at 12 mm.	(3)
147°	at 12 mm.	(4)
143–147°	at 12 mm.	(5)

$D_4^{20.8} = $ **1.1718** (3) $n_D^{20.6} = $ **1.46847** (3)

[For prepn. of $\bar{C}$ from suberic acid (1:0755) with PCl_5 (1), with PCl_3 (4), or with $SOCl_2$ (yield: 100% (2)) (3) (5) (6) (8) (10) see indic. refs.]

[$\bar{C}$ with excess MeOH yields (6) dimethyl suberate (1:4186), b.p. 268°. $\bar{C}$ with 1 mole MeOH should yield 7-carbomethoxyheptanoyl chloride-1, b.p. 163–165° at 34 mm. (7), usually prepd. from methyl hydrogen suberate with $SOCl_2$ (7).]

$\bar{C}$ with excess phenol htd. at 100° yields (8) diphenyl suberate, m p. 70–71° (8).

$\bar{C}$ htd. with dry disodium suberate yields (1) suberic anhydride, m.p. 65–66° (1), presumably the linear polymeric suberic α-anhydride (cf. 1:0755).

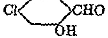
$\bar{C}$ with $AlCl_3$ + C_6H_6 yields (1) (4) 1,8-diphenyloctanedione-1,8, m.p. 85° (4), 83–85° (1) (dioxime, m.p. 192–193° (1)).

[$\bar{C}$ on cat. hydrogenation over Pd/diatomaceous earth as directed (9) yields suberic dialdehyde (octanedial-1,8), (*bis*-oxime, m p. 152° (9), *bis*-phenylhydrazone, m.p. 84–86° u.c. (9), *bis*-semicarbazone, m.p. 183–186° (9)) cf. (2).]

$\bar{C}$ converted to RMgCl (as above) and treated with ethereal $HgCl_2$ gives (35% yield (1)) 2,2,3,3-tetramethylbutyl mercuric chloride, *feathery white cryst.*, m.p. *170–171°* (1).

3:0945 (1) Whitmore, Marker, Plambeck, *J. Am. Chem. Soc.* **63**, 1626–1630 (1941).

3:0960 4-CHLORO-2-HYDROXYBENZALDEHYDE $C_7H_5O_2Cl$ **Beil. No. 744**
(4-Chlorosalicylaldehyde)



M.P. 52.5° (1)

Long colorless ndls. from alc. or dil. AcOH (1). — $\bar{C}$ has odor of walnuts (1). — $\bar{C}$ is apprec sol. in aq. or aq. H_2SO_3; readily sol. in org. solvents. — $\bar{C}$ is very volatile with steam even from its yel. soln. in alk. (1).

[For prepn. of $\bar{C}$ from *m*-chlorophenol (3.0255) via Reimer-Tiemann procedure see (1).]

$\bar{C}$ does not reduce $NH_4OH/AgNO_3$ or Fehling soln.; is very resistant to oxidn. by acid, alk., or neutral $KMnO_4$, and to acetylation (but not benzoylation, q.v. below) (1).

$\bar{C}$ with $FeCl_3$ gives brown ppt., with $CuSO_4$ or $Cr_2(SO_4)_3$ + dil. aq. alk. gives bright green copper salt and a dark green chromium salt (1).

$\bar{C}$ on mononitration as specified (2) yields 5-nitro-4-chloro-2-hydroxybenzaldehyde, pale yel. ndls. from alc., m.p. 116° (2) [*This product yields a phenylhydrazone, or.-yel. ndls.*, m.p. 188° dec.; a *p*-nitrophenylhydrazone, brn.-yel. ndls from alc. or AcOH, m.p. 294° dec.; and a semicarbazone, pale yel. ndls from dil. AcOH, dec. above 300° (2).]

$\bar{C}$ on dinitration as specified (2) yields 3,5-dinitro-4-chloro-2-hydroxybenzaldehyde, pale gold.-yel. ndls. from aq., m.p. 153° (2). [This product yields a phenylhydrazone, light brn. cryst. from alc., m.p. 219°; a *p*-nitrophenylhydrazone, light brn. cryst. from dil. AcOH, m.p. 286° dec.; and a semicarbazone, light yel. cryst. from dil. AcOH, m.p. 225° dec. (2).]

Ⓓ **4-Chloro-2-hydroxybenzaldoxime**: colorless ndls. from alc., m.p. 155° (1).

Ⓓ **4-Chloro-2-hydroxybenzaldehyde *p*-nitrophenylhydrazone**: or. ndls. from AcOH, m.p. 257° (1).

Ⓓ **4-Chloro-2-hydroxybenzaldehyde semicarbazone**: pale yel. cryst. from AcOH, m.p. 212° (1).

Ⓓ **4-Chloro-2-benzoxybenzaldehyde**: from $\bar{C}$ + BzCl in ether + pyridine; ndls. from alc., m.p. 98.5° (1).

3:0960 (1) Hodgson, Jenkinson, *J. Chem. Soc.* **1927**, 1740–1741. (2) Hodgson, Jenkinson, *J. Chem. Soc.* **1928**, 2273–2274.

3:9590 8-CHLORO-OCTANOL-1 $CH_2(CH_2)_6.CH_2OH$ (with Cl on the first CH_2) $C_8H_{17}OCl$ Beil. S.N. 24
(ω-Chloro-*n*-octyl alcohol)

B.P. 139° at 18.5 mm. (1)
125–140° at 18 mm. (2)

[For prepn. of C̄ from α,ω-octamethylene glycol (m.p. 63°, b.p. 167–168° at 18 mm. (2)) with conc. HCl as directed (yields: 81% (2), 75% (1), 65% (3)) see indic. refs.]

C̄ with thiophenol in aq. NaOH htd. 3 hrs. gives (2) 8-hydroxy-*n*-octyl phenyl sulfide, pl from lt. pet., m p. 55° [this prod. with $SOCl_2$ gives (2) 8-chloro-*n*-octyl phenyl sulfide, cryst. from aq. alc. at low temp., m.p. 16°].

[C̄ (1 mole) with Et_2NH (3–4 moles) in s t. at 120–160° for 12–15 hrs. gives (88% yield (1)) 8-(diethylamino)octanol-1, b.p. 151° at 12 mm., $D_4^{15.5} = 0.8610$, $n_D^{19} = 1.4570$ (1) cf. (5) (corresp. *p*-nitrobenzoate, m.p. 74° (1)); this prod. with $SOCl_2$ in C_6H_6 yields (1) (5) 8-(diethylamino)-*n*-octyl chloride, b.p. 130.5° at 11 mm., $n_D^{18} = 1.4535$ (1) cf. (5) (corresp B̄.HCl, m.p. 73° (5)).]

C̄ with morpholine gives (4) alm. quant. 8-(4-morpholinyl)octanol-1, b.p. 164.0–164 2° at 5 mm., $D_4^{25} = 0.9675$, $n_D^{27} = 1.4735$ (corresp. *N*-(α-naphthyl)carbamate, m.p. 73.0–74.0° cor.) — C̄ (1 mole) with *N*-phenylpiperazine (2 moles) at 100° for 5 hrs. gives (3) in alm. 100% yield (as salt) *N*-(8-hydroxy-*n*-octyl)-*N'*-phenylpiperazine, m p. 57.0–58 5° cor. (corresp. *N*-phenylcarbamate, m.p. 99.5–100.5° cor.); note that this free base readily absorbs aq. from air to form a monohydrate, m.p. 80–82° (3).

Ⓓ 8-Chloro-*n*-octyl *N*-phenylcarbamate: ndls from aq. alc., m.p. 77° (2).
Ⓓ 8-Chloro-*n*-octyl *N*-(*m*-nitrophenyl)carbamate: m.p. 62° (1).

3:9590 (1) Altman, *Rec. trav. chim.* **57**, 951–952 (1938). (2) Bennett, Mosses, *J. Chem. Soc.* **1931**, 1698–1701. (3) Anderson, Pollard, *J. Am Chem. Soc* **61**, 3439–3440 (1939). (4) Anderson, Pollard, *J. Am. Chem. Soc.* **61**, 3440–3441 (1939). (5) Pyman, Levene (to Boot's Pure Drug Co.), Brit. 402,159, Dec. 21, 1933; *Cent.* **1934**, I 2005, *C.A.* **28**, 3081 (1934).

3:9594 β-CHLORO-*n*-BUTYRALDEHYDE DIETHYLACETAL $C_8H_{17}O_2Cl$ Beil. I - 663
$CH_3CH.CH_2.CH(OC_2H_5)_2$ (with Cl on the CH) I_1—
(β-Chlorobutyracetal) I_2-(724)

B.P. 70–71° at 12 mm. (1) $D_4^{20} = 0.9677$ (2) $n_D^{20} = 1.42103$ (2)

Oil insol. aq.; misc. with alc., C_6H_6, AcOH, or $CHCl_3$ or pet. ether.

[For prepn. of C̄ from crotonaldehyde (1:0150) with abs. EtOH + dry HCl (yield: 66% (1), 50% (3)) (2) see indic. refs.]

C̄ on distn. with dry KOH gives (70–80% yield) crotonaldehyde diethylacetal [Beil. I-730, I_1-(380), I_2-(789)], b.p. 146–148°.

[For reactn. of C̄ with alc. NH_3 in s.t. at 120–130° giving (20% yield (4)) β-amino-*n*-butyraldehyde diethylacetal see (4); for analogous behavior of C̄ with other amines see (4) (3).]

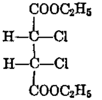
3:9594 (1) Wohl, Frank, *Ber.* **35**, 1905–1906 (1902). (2) Wichterle, Vavrecka, *Collection Czech-oslov. Chem. Commun.* **10**, 494 (1938). (3) Mason, *J. Chem. Soc.* **127**, 1033 (1925). (4) Mannich, Horkheimer, *Arch. Pharm.* **264**, 171–172 (1926).

$\bar{C}$ treated with Br_2, then poured into abs. formic acid and boiled until evolution of CO ceases, yields (10) α,α'-dibromosuberic acid, m.p. 172–173° (10). [From the mother liq. a small amt. of another form, m p. 120–121° (10), can be obtd.]

$\bar{C}$ on hydrolysis yields suberic acid (1:0755), m p. 141° (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to $\bar{C}$ see 1:0755).

3:9576 (1) Etaix, *Ann chim.* (7) **9**, 386–391 (1896). (2) Fröschl, Maier, *Monatsh.* **59**, 273–274 (1932). (3) von Auwers, Schmidt, *Ber.* **46**, 479 (1913). (4) Borsche, Wolleman, *Ber.* **45**, 3717 (1912). (5) Blaise, Koehler, *Bull. soc. chim.* (4) **5**, 690 (1909). (6) Meyer, *Monatsh.* **22**, 421 (1901). (7) Morgan, Walton, *J. Chem Soc* **1935**, 292. (8) Marangoni, *Atti ist. Veneto sci. Pt.* 2. *Sci. math. nat* **97**, 209–218 (1937–1938), *Cent.* **1939**, I 96; *C.A.* **34**, 6934–6935 (1940). (9) Rosenmund, Zetsche, *Ber.* **54**, 2889–2890 (1921). (10) Goss, Ingold, *J. Chem. Soc.* **1926**, 1473.

3:9578 DIETHYL *d,l*-α,α'-DICHLOROSUCCINATE $C_8H_{12}O_4Cl_2$ **Beil. II - 620**
(Diethyl *allo*-dichlorosuccinate; diethyl isodichlorosuccinate) II_1— II_2-(558)



B.P. 132° cor. at 15 mm. (1)
129.5° at 12.5 mm. (1)

D_4^{99} = **1.1636** (1) $n_D^{64.5}$ = **1.4296** (1)
D_4^{77} = **1.1963** (1) n_D^{20} = **1.4512** (1)
$n_D^{17.5}$ = **1.4521** (1)

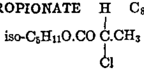
Stable oil (1), contrary to earlier (2) report.

[For prepn. of $\bar{C}$ from *d,l*-α,α'-dichlorosuccinic acid (3:4711) in EtOH with HCl gas see (1) cf. (2).]

$\bar{C}$ with 30% H_2SO_4 on boilg. not only hydrolyzes but also loses HCl yielding (3) chlorofumaric acid (3:4853).

3:9578 (1) Kuhn, Wagner-Jauregg, *Ber.* **61**, 485–486, 504 (1928). (2) van der Riet, *Ann.* **280**, 221 (1894). (3) Patterson, Todd, *J. Chem. Soc.* **1929**, 1769–1770.

3:9580 ISOAMYL *d,l*-α-CHLOROPROPIONATE $C_8H_{15}O_2Cl$ **Beil. S.N. 162**

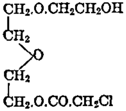


B.P.——

D_4^{20} = **1.0050** (1) n_D^{20} = **1.4289** (1)

3:9580 (1) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

3:9588 β-[(β-HYDROXYETHOXY)ETHOXY]-ETHYL CHLOROACETATE $C_8H_{15}O_5Cl$ **Beil. S.N. 160**
[Triethylene glycol mono(chloroacetate)]

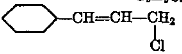


B.P. 180–195° at 0.5 mm. (1)

Viscous oil, insol. in aq. but slowly dissolving when shaken with aq. because of hydrolysis to triethylene glycol (1:6538) + chloroacetic ac. (3:1370) (1).

3:9588 (1) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 317 (1933).

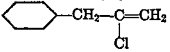
—— CINNAMYL CHLORIDE (3-Chloro-1-phenylpropene-1) C_9H_9Cl Beil. V-(482) V_1-(232) V_2-(372)



B.P. 140° at 37 mm. M.P. 8–9° $D_4^{25} = 1.08815$ $n_D^{25} = 1.58065$

See 3:0010. *Division A: Solids.*

3:9608 2-CHLORO-3-PHENYLPROPENE-1 C_9H_9Cl Beil. S.N. 473



B.P. 105–107° at 26 mm. (1)

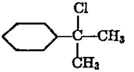
[For prepn. of C̄ from benzyl methyl ketone (phenylacetone) (1:5118) with PCl_5 in C_6H_6 (yield 45.9% accompanied by 26.3% of the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)) see (1).]

C̄ on stdg. isomerizes in part to the mesomeric 2-chloro-1-phenylpropene-1 (3:9606)(1).

C̄ (freshly distilled) with O_3 in $CHCl_3$ contg. some EtOH yields (1) ethyl phenylacetate (1:3872) (note difference from the mesomer).

3:9608 (1) Zaki, Iskander, *J. Chem. Soc.* **1943**, 68–69.

3:9610 α-CHLORO-ISOPROPYLBENZENE (Dimethyl-phenyl-carbinyl chloride; 2-chloro-2-phenylpropane) $C_9H_{11}Cl$ Beil. V - 395 V_1— V_2 - (307)



No physical constants for C̄ appear to have been reported, presumably because of its ease of decomposition.

[For prepn. of C̄ from dimethyl-phenyl-carbinol [Beil. VI-506] by saturation with dry HCl gas at 0° see (1) (2).]

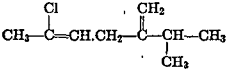
C̄ on htg evolves HCl (1). — C̄ in C_6H_6 + $SnCl_4$ stood for several hours below 10° gives (88% yield) the "saturated dimer of α-methylstyrene," i.e., 1,1,3-trimethyl-3-phenylhydrindene, cryst. from alc., m.p. 52° (3).

C̄ on slow addn. to boilg. alc. KOH (4) or on warming with pyridine (1) (4) loses HCl smoothly giving (70% yield (5)) α-methylstyrene (β-phenylpropylene) [Beil. V-484, V_1-(233)], b.p. 161–162° (5).

C̄ dislvd. in MeOH and merely stood overnight gives (6) the corresponding ether, viz., 2-methoxy-2-phenylpropane, b.p. 78° at 13 mm., $D_4^{20} = 0.945$, $n_D^{20} = 1.4981$ (6).

2546 (1929). (3)
ı. (8) **10**, 156–157
i4–255 (1924).

3:9614 2-CHLORO-6-METHYL-5-METHYLENEHEPTENE-2 $C_9H_{15}Cl$ Beil. S.N. 10



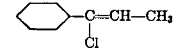
B.P. 95–96° at 18 mm. (1) $D_4^{25} = 0.9310$ (1) $n_D^{25} = 1.4730$ (1)

CHAPTER XXII

DIVISION C. LIQUIDS WITH BOILING POINTS REPORTED ONLY UNDER REDUCED PRESSURE

3:9600–3:9999 (C_9–C_{18} inclusive)
(Arranged in sequence of empirical formulas)

3:9604 1-CHLORO-1-PHENYLPROPENE-1 C_9H_9Cl **Beil. V —**
(α-Chloro-β-methylstyrene) **V_1-(232)**
V_2-(372)



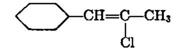
B.P. 90.5° at 9 mm. (1) $D_4^{20} = 1.085$ **(1)**
$D_4^{14.8} = 1.0890$ **(1)** $n_D^{14.6} = 1.56352$ **(1)**

[For prepn of C̄ from ethyl phenyl ketone (propiophenone) (1:5525) by treatment with PCl_5 followed by alc. KOH see (1).]

[C̄ with $NaNH_2$ in toluene at 110° gives traces (2) of methyl-phenyl-acetylene [Beil. V-514, V_2-(408)].]

3:9604 (1) von Auwers, *Ber.* **45**, 2799–2801 (1912). (2) Bourgeul, *Ann chim.* (10) **3**, 351 (1925).

3:9606 2-CHLORO-1-PHENYLPROPENE-1 C_9H_9Cl **Beil. S.N. 473**
(β-Chloro-β-methylstyrene)



B.P. 118–123° at 28 mm. (1) $D_4^{19} = 1.0738$ **(3)** $n_D^{19} = 1.5565$ **(3)**
120–124° at 26 mm. (2) $D_4^{0} = 1.0912$ **(3)**
61.5–62.5° at 2 mm. (3)

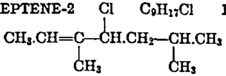
[For prepn. of C̄ from benzyl methyl ketone (phenylacetone) (1:5118) with PCl_5 in C_6H_6 (26.3% yield accompanied by 45.9% of the mesomeric 2-chloro-3-phenylpropene-1 (3:9608)) see (2); from 2,3-dichloro-1-phenylpropene-1 (3) by partial reduction with Zn dust in EtOH under N_2 (70% yield accompanied by 16–20% 1-phenylpropadiene-1,2 (phenylallene)) see (3); for formn. as by-prod. during addn. of HOCl to α-methylcinnamic acid see (1).]

Note that C̄ on stdg isomerizes in part (2) to the mesomeric 2-chloro-3-phenylpropene-1 (3:9608).

C̄ (freshly distilled) with O_3 in $CHCl_3$ gives (2) benzoic acid (1:0715); C̄ on oxidn. with $KMnO_4$ yields (3) benzoic acid (1:0715) + AcOH (1:1010) (note difference from the mesomer).

3:9606 (1) Hose, Farmer, *J. Chem Soc* **1933**, 965. (2) Zaki, Iskander, *J. Chem. Soc.* **1943**, 68–69 (3) Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1029–1041 (1938); *Cent.* **1939**, I 2183; *C.A.* **33**, 3776 (1939).

3:9630 4-CHLORO-3,6-DIMETHYLHEPTENE-2 $C_9H_{17}Cl$ Beil. I — I_1 - (95) I_2—

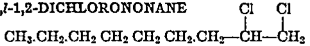


B.P. 59–63° at 9 mm. (1)

[For prepn. of C̄ from 2,5-dimethylhepten-5-ol-4 [Beil. I_1-(231)] with .6 *N* HCl (78% yield) see (1).]

3:9630 (1) Abelmann, *Ber.* **43**, 1582 (1910).

3:9632 *d,l*-1,2-DICHLORONONANE $C_9H_{18}Cl_2$ Beil. S.N. 10

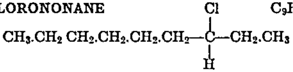


No data on C̄ have apparently been reported.

[For prepn. of C̄ from nonene-1 (1:8385) by actn. of HOCl (together with 1-chlorononanol-2) see (1).]

3:9632 (1) Kiss (to Shell Development Co.), U.S. 1,767,291, June 24, 1930; *Cent.* **1930**, II 1475.

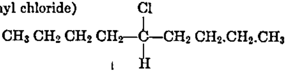
3:9638 *d,l*-3-CHLORONONANE $C_9H_{19}Cl$ Beil. S.N. 10



C̄ has not as yet been reported, although both the optical isomerides are known. The dextrorotatory form of C̄, *from levorotatory nonanol-3 with HCl at 100° (1), or from* levorotatory 3-iodononane with LiCl in MeOH (2), has b.p. 98° at 33 mm. (2), 87–89° at 24 mm. (1), D_4^{17} = 0.8588 (1). The levorotatory form of C̄, from dextrorotatory nonanol-3, with HCl at 100° (1), has b.p. 101° at 40 mm., D_4^{17} = 0.8540 (1).

3:9638 (1) Pickard, Kenyon, *J. Chem. Soc.* **99**, 71 (1911). (2) Levene, Rothen, Kuna, *J. Biol. Chem.* **120**, 786 (1937).

3:9640 *d,l*-5-CHLORONONANE $C_9H_{19}Cl$ Beil. I — I_1— I_2 - (128)
(Di-*n*-butylcarbinyl chloride)

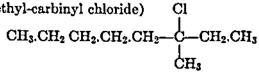


B.P. 85–87° at 14 mm. (1) D_4^{15} = **0.8639 (1)** n_D^{15} = **1.4314 (1)**

[For prepn. of C̄ from 5-bromononane by conversion to RMgBr and subsequent treatment with Cl.CN (68% yield) see (1).]

3:9640 (1) Grignard, Ono, *Bull soc. chim.* (4) **39**, 1592 (1926).

3:9642 *d,l*-3-CHLORO-3-METHYLOCTANE $C_9H_{19}Cl$ Beil. S.N. 10
(*n*-Amyl-ethyl-methyl-carbinyl chloride)



B.P. 72.7–74.0° at 15 mm. (1) D_4^{25} = **0.8680 (1)** n_D^{25} = **1.4330 (2)**
n_D^{20} = **1.4351 (2)**
1.4347 (1)

[For prepn. of C̄ from 2-methyl-3-methyleneheptanone-6 (thujaketone) [Beil. I-745, I_1-(386)] with PCl_5 in the cold, then htd. at 100° for 2½ hrs. (40% yield), see (1).]
C̄ on oxidn. with $KMnO_4$ yields (1) 2-methylbutanone-3 (isopropyl methyl ketone) (1:5410) q.v.

3:9614 (1) Werner, Bogert, *J. Org. Chem.* **3**, 585 (1939).

3:9618 1-CHLORONONYNE-1 $C_9H_{15}Cl$ Beil. S.N. 12

$$CH_3\,CH_2\,CH_2.CH_2.CH_2\,CH_2\,CH_2.C{\equiv}C\text{—}Cl$$

B.P. 75–77° at 15 mm. (1) $D^{20}_{-} = 0.906$ (1) $n^{20}_D = 1.450$ (1)

[For prepn. of C̄ from nonyne-1 (1:8125) by conversion with $NaNH_2$ to C_7H_{15}—C≡C—Na and subsequent reactn. with benzenesulfonyl chloride in dry ether (55% yield (1)) see (1).]
[Refractive indices of C̄ by Pulfrich instrument: $n^{13}_C = 1.4492$, $n^{13}_D = 1.4519$, $n^{13}_F = 1.4582$, $n^{13}_G = 1.4634$ (1).]

3:9618 (1) Truchet, *Ann. chim.* (10) **16**, 335, 337 (1931).

3:9622 *d,l*-2-CHLORO-2-METHYLOCTYNE-3 $C_9H_{15}Cl$ Beil. S.N. 12

$$CH_3.CH_2.CH_2\,CH_2\text{—}C{\equiv}C\text{—}C(Cl)(CH_3)\text{—}CH_3$$

B.P. 68° at 15 mm. (1) $D^{20}_4 = 0.8929$ (1) $n^{20}_D = 1.4480$ (1)

[For prepn. of C̄ from 2-methyloctyn-3-ol-2 (1) by saturation with HCl gas (85% yield) see (1).]
[C̄ with MeMgBr gives 74% yield 2,2-dimethyloctyne-3, b.p. 79° at 70 mm., $D^{20}_4 = 0.7491$, $n^{20}_D = 1.4270$ (1); C̄ with EtMgBr gives 60% yield 3,3-dimethylnonyne-4, b.p. 82° at 40 mm., $D^{20}_4 = 0.7650$, $n^{20}_D = 1.4312$ (1).]

3:9622 (1) Campbell, Eby, *J. Am. Chem. Soc.* **62**, 1799–1800 (1940).

3:9624 5-CHLORO-4-METHYLOCTENE-3 $C_9H_{17}Cl$ Beil. I — I_1 - (95) I_2—

$$CH_2\,CH_2\,CH_2\text{—}CH(Cl)\text{—}C(CH_3){=}CH.CH_2.CH_3$$

B.P. 59–62° at 11 mm. (1)

[For prepn. of C̄ from 4-methylocten-3-ol-5 [Beil. I_1-(230), I_2-(492)] with conc. HCl see (1).]

3:9624 (1) Bjelouss, *Ber.* **45**, 626 (1912).

3:9628 *d,l*-4-CHLORO-7-METHYLOCTENE-2 (Isoamyl-propenyl-carbinyl chloride; 5-chloro-2-methyloctene-6) $C_9H_{17}Cl$ Beil. I - 223 I_1— I_2—

$$CH_3.CH{=}CH\text{—}CH(Cl).CH_2\,CH_2\text{—}C(CH_3)(H)\text{—}CH_3$$

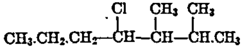
B.P. 124–126° at 108 mm. (1)

[For prepn. of C̄ from 2-methylocten-6-ol-5 (isoamyl-propenyl-carbinol) [Beil. I-449, I_1-(230), I_2-(492)] with PCl_5 see (1).]

3:9628 (1) Reif, *Ber.* **41**, 2740, 2743, Note 1 (1908).

3:9650 3-CHLORO-2,3-DIMETHYLHEPTANE $C_9H_{19}Cl$ Beil. S.N. 10

(*n*-Butyl-isopropyl-methyl-carbinyl chloride)



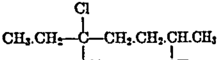
B.P. 54° at 8 mm. (1) $D_4^{23} = 0.8809$ (1)
$D_4^{20} = 0.885$ (1) $n_D^{20} = 1.4391$ (1)

[For prepn. of $\bar{C}$ from 2,3-dimethylheptanol-3 (*n*-butyl-isopropyl-methyl-carbinol) (1) with dry HCl at 0° (86% yield) see (1).]

3:9650 (1) Whitmore, Evers, *J. Am. Chem. Soc.* **55**, 813 (1933).

3:9652 *d,l*-5-CHLORO-2,5-DIMETHYLHEPTANE $C_9H_{19}Cl$ Beil. I — I_1-(64) I_2—

(Ethyl-isoamyl-methyl-carbinyl chloride)



B.P. 63–64° at 15 mm. (1) $D_4^{18.5} = 0.8692$ (1) $n_D^{15} = 1.43457$ (1)

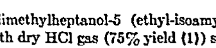
[For prepn. of $\bar{C}$ from 2,5-dimethylheptanol-5 (ethyl-isoamyl-methyl-carbinol) [Beil. I-425, I_1-(212)] by saturation with dry HCl gas (75% yield (1)) see (1).]

[$\bar{C}$ with $AlCl_3 + C_6H_6$ yields (1) 5-phenyl-2,5-dimethylheptane, b.p. 122–123° at 14 mm, $D_4^{16} = 0.8788$, $n_D^{13} = 1.49894$ (1).]

3:9652 (1) Halse, *J. prakt. Chem.* (2) **89**, 455 (1914).

3:9654 *d,l*-3-CHLORO-2,2,3-TRIMETHYLHEXANE $C_9H_{19}Cl$ Beil. S.N. 10

(*ter*-Butyl-methyl-*n*-propyl-carbinyl chloride)



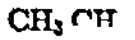
B.P. 64.2–65.5° at 12.5–13 mm. (1) (1)

[For prepn. of $\bar{C}$ from 2,2,3-trimethylhexanol [Beil. I_2-(458)] (1) by saturation with dry HCl at 0°

3:9654 (1) Petrov, Karasev, Cheltzova, *Bull. soc.*

3:9656 3-CHLORO-2,2-DIMETHYL

(*ter*-Butyl-diethyl-carbinyl chloride)



B.P. 53–54° at 6 mm. (1)

[For prepn. of $\bar{C}$ from 2,2-dimethyl-3-
(1) with dry HCl gas at 0° see (1).]

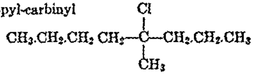
$\bar{C}$ on distn. at 150 mm. loses HCl (1) yielding a

3:9656 (1) Bartlett, Knox, *J. Am. Chem. Soc.* **61**,

[For prepn. of C̄ from 3-methyloctanol-3 (*n*-amyl-ethyl-methyl-carbinol) (1) with HCl gas (72% yield) see (1).]

3:9642 (1) Whitmore, Williams, *J. Am. Chem. Soc.* **55**, 408–409 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc.* **67**, 21 (1945).

3:9644 ***d,l*-4-CHLORO-4-METHYLOCTANE** $C_9H_{19}Cl$ **Beil. S.N. 10**
(*n*-Butyl-methyl-*n*-propyl-carbinyl chloride)

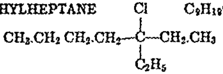


B.P. 70.8–71.4° at 14.5 mm. (1) $D_4^{25} = 0.8690$ (1) $n_D^{25} = 1.4338$ (2)
$D_4^{20} = 0.8723$ (1) $n_D^{20} = 1.4360$ (2)
1.4349 (1)

[For prepn. of C̄ from 4-methyloctanol-4 (*n*-butyl-methyl-*n*-propyl-carbinol) {Beil. I₁-(211)} (1) with dry HCl at −10° see (1).]

3:9644 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* **55**, 363–364 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc* **67**, 21 (1945).

3:9646 ***d,l*-3-CHLORO-3-ETHYLHEPTANE** $C_9H_{19}Cl$ **Beil. S.N. 10**
(*n*-Butyl-diethyl-carbinyl chloride)

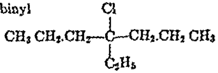


B.P. 46.0° at 3 mm. (1) $D_4^{25} = 0.8822$ (1)
$D_4^{20} = 0.8856$ (1) $n_D^{20} = 1.4400$ (1)

[For prepn. of C̄ from 3-ethylheptanol-3 (*n*-butyl-diethyl-carbinol) {Beil. I_1-(211), I_2-(457)} (1) with dry HCl gas at −10° see (1).]

3:9646 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* **55**, 363–364 (1933).

3:9648 **4-CHLORO-4-ETHYLHEPTANE** $C_9H_{19}Cl$ **Beil. I —**
(Ethyl-di-*n*-propyl-carbinyl chloride) I_1 - (64)
I_2—



B.P. 67–68° at 12 mm. (1) $D_4^{20} = 0.8821$ (1) $n_D^{20} = 1.4438$ (2)
62–64° at 10 mm. (2) $D_4^{16} = 0.884$ (2) $n_D^{15} = 1.43878$ (1)

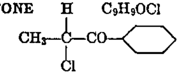
[For prepn. of C̄ from 4-ethylheptanol-4 (ethyl-di-*n*-propyl-carbinol) {Beil. I-424, I_1-(212), I_2-(457)} by saturation with HCl gas see (1); for formn. of C̄ from 3-*n*-propylhexene-2 (2) with conc. HCl see (2).]

[For data on density and parachor of C̄ at 0°, 15°, 25°, and 65° see (3).]

[C̄ with $AlCl_3$ + C_6H_6 gives 67% yield 4-ethyl-4-phenylheptane, b.p. 127–128° at 15 mm., $D_4^{20} = 0.8698$, $n_D^{15} = 1.49211$ (1).]

3:9648 (1) Halse, *J. prakt. Chem.* (2) **89**, 456–457 (1914). (2) Nasarov, *Ber.* **70**, 624 (1937). (3) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3107–3111 (1939).

3:9664 α-CHLOROETHYL PHENYL KETONE C_9H_9OCl Beil. S.N. 640
(α-Chloropropiophenone)

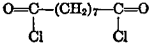


B.P. 131–133° at 26 mm. (1)

[For prepn. (66.4% yield (1)) from α-chloropropionyl chloride (3:5320) + C_6H_6 + $AlCl_3$ see (1).]

3:9664 (1) *Baker, Barkenbus, J. Am. Chem. Soc.* **58**, *263 (1936).*

3:9680 AZELAYL (DI)CHLORIDE $C_9H_{14}O_2Cl_2$ Beil. II - 709
II_1—
II_2—



B.P. 180–183° at 35 mm. (1)
166° at 18 mm. (2)
165° at 13 mm. (1)
140° at 0.4 mm. (3)

[For prepn. of C̄ from azelaic acid (1:0695) with PCl_5 (1) or with $SOCl_2$ (2) (3) see indic. refs.]

[C̄ with 1 mole MeOH should yield 8-carbomethoxyoctanoyl chloride-1, b.p. 150–155° at 15 mm. (7), usually prepd. from methyl hydrogen azelate, b.p. 190–195° at 15 mm., m.p. 21–24° (7), with $SOCl_2$ (7).]

C̄ on htg. with disodium azelate yields (1) azelaic anhydride, m.p. 54–56° (1) (this prod. *is probably the linear polymeric α-anhydride (see 1:0695)).*

[C̄ with C_6H_6 + $AlCl_3$ yields (1) 1,9-diphenylnonanedione-1,9, m.p. 44° (1); C̄ with toluene + $AlCl_3$ yields (4) 1,9-di-*p*-tolylnonanedione-1,9, m.p. 78–79° (4).]

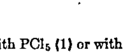
C̄ with phenol yields (5) (6) diphenyl azelate, m p 59–60° (6), 49–50° (5).

[C̄ with MeZnI yields (2) undecanedione-2,10, m.p. 64° (2).]

C̄ on hydrolysis yields azelaic acid (1:0695), m.p. 106° (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to C̄ see 1:0695).

3:9680 (1) Etaix, *Ann. chim.* (7) **9**, 397–401 (1896). (2) Blaise, Koehler, *Bull. soc. chim.* (4) **5**, 692 (1909). (3) Ruzicka, Boekenoogen, *Helv Chim Acta* **14**, 1332 (1931). (4) Borsche, *Ber.* **52**, *2081–2082 (1919).* (5) *Bouchonnet, Compt. rend.* **140**, *1599 (1905).* (6) *Marangoni, Atti ist. Veneto sci. Pt.* 2, *Sci. math. nat.* **97**, 209–218 (1937–38); *Cent.* **1939**, I 96; *C.A.* **34**, 6934–6935 (1940). (7) Morgan, Walton, *J. Chem. Soc.* **1936**, 903.

3:9701 2,3,6-TRIMETHYLBENZYL CHLORIDE $C_{10}H_{13}Cl$ Beil. S.N. 469



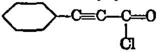
This compound is apparently unreported although the corresp. 2,3,6-trimethylbenzyl bromide, b.p. 146° at 23 mm., 130–132° at 14 mm., has been obtd. (41% yield (1)) from prehnitene (1,2,3,4-tetramethylbenzene) (1:7548) by bromination.

Certain derivatives of C̄ are, however, recorded here because of the desirability of comparison with the corresp. derivs. of 2,4,5-trimethylbenzyl chloride (3:9702) and of 2,4,6-trimethylbenzyl chloride (3:0372).

—— **2,3,6-Trimethylbenzyl alcohol:** m.p. 83.5–85° (1).
—— **2,3,6-Trimethylbenzyl acetate:** oil, b.p. 152° at 23 mm. (1).

3:9701 (1) *Smith, Agre, J. Am. Chem Soc.* **60**, *652–653 (1938).*

3:9658 PHENYLPROPIOLYL CHLORIDE C_9H_5OCl Beil. IX - 635
IX_1—



B.P. 130–133° at 25–30 mm. (1)
115–116° at 17 mm. (2)
119° at 12 mm. (3)

[For prepn. of $\bar{C}$ from phenylpropiolic acid (1:0745) with PCl_5 (1) (2) cf. (3), or refluxed with 7 pts $SOCl_2$ (90–95% yield (4)) (3), or from sodium propiolate (available from pharmaceutical industry (5)) with $SOCl_2$ (5) but not PCl_3 (2), see indic. refs. Note that phenylpropiolic acid (1:0745) dislvd. in 2 pts. $POCl_3$ at 100° and htd. 3 min. beyond first sepn. of cryst. (6), or the acid refluxed with Ac_2O (7), gives good yield 1-phenylnaphthalene-2,3-dicarboxylic anhydride [Beil. XVII-541, $XVII_1$-(275)], ndls. from C_6H_6 + lgr., m p. 255°.]

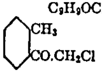
[For reactn. of $\bar{C}$ with $AlCl_3$ + anisole (1:7445) yielding (1) (3) *p*-methoxyphenyl phenylethynyl ketone [Beil. VIII-199], m.p. 100° (1) (3) (dibromide, m.p. 138–140° (3)), see indic. refs.; for reactn. of $\bar{C}$ with $AlCl_3$ + methyl *p*-tolyl ether (1:7495) giving (60% yield (5)) 2-hydroxy-5-methyl-β-chlorochalcone, deep yel. ndls. from pet. eth., m.p. 95 5° (which in alc. on dropwise treatment with dil. aq. NaOH ring-closes by loss of HCl to give quant. (5) 6-methylflavone [Beil. $XVII_1$-(206)], m.p. 122° (5)), see (5); for reactn. of $\bar{C}$ with $AlCl_3$ + resorcinol (1:1530) in nitrobenzene to give 7-hydroxyflavone [Beil. XVIII-58], m p. 241°, see (8).]

[For reactn. of $\bar{C}$ with diethyl sodio-malonate (4), ethyl sodio-acetoacetate (4), sodio-acetylacetone (4), with Na phenylacetylene or phenyl-ethynyl MgBr (9) see indic. refs.]

$\bar{C}$ on hydrolysis (presumably) yields phenylpropiolic acid (1:0745), m.p. 136°. For the amide, anilide, *p*-toluidide, and other derivs. corresp. to $\bar{C}$ see the acid (1:0745).

3:9658 (1) Stockhausen, Gattermann, *Ber.* **25**, 3537–3538 (1892). (2) Rupe, *Ann.* **369**, 329 (1909). (3) Watson, *J. Chem. Soc.* **85**, 1324–1325 (1904). (4) Ruhemann, Merriman, *J. Chem. Soc.* **87**, 1389–1395 (1905). (5) Simonis, Lear, *Ber.* **59**, 2908–2913 (1926). (6) Michael, *Ber.* **39**, 1911–1912 (1906). (7) Michael, Bucher, *Am. Chem. J.* **20**, 91–92 (1898). (8) Seka, Prosche, *Monatsh.* **69**, 289 (1936). (9) Hess, Weltzien, *Ber.* **54**, 2515–2516 (1921).

3:9660 *o*-METHYLPHENACYL CHLORIDE C_9H_9OCl Beil. S.N. 640
(Chloromethyl *o*-tolyl ketone;
ω-chloro-*o*-methylacetophenone)



B.P. 129–130° at 11 mm. (1)

Clear pale yel. liq. (1). — Strong lachrymator!

[For prepn. from benzyl MgCl + chloroacetic acid anhydride (3:0730) (42% yield (1)) see (1); from *o*-toluyl chloride (3:8740) + diazomethane see (2).]

$\bar{C}$ on oxidn. with NaOCl gives (56% yield (1)) *o*-toluic ac. (1:0690), m.p. 104° (1).

① Chloromethyl *o*-tolyl ketone semicarbazone: m.p. 103–105° (1).

3:9660 (1) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 656 (1932). (2) Mercer, Robertson, Cahn, *J. Chem. Soc.* **1935**, 1000.

— *p*-CHLOROPHENYL ETHYL KETONE C_9H_9OCl Beil. VII - 301
VII_1—

B.P. 152° at 30 mm. M.P. 35–36°

See 3:0340. *Division A: Solids.*

3:0980 *p*-DICHLOROBENZENE ClCl $C_6H_4Cl_2$ Beil. V - 203
V_1-(111)
V_2-(154)

M.P.		B.P.		
55°	(1) (51)	174°	at 764.2 mm. (24)	$D_4^{80.3}$ = 1.2189 (33)
54° (2), cor.	(3)	173.7°	cor. (5)	$n_D^{80.3}$ = 1.52104 (33)
53.3–54.2°	(4)	173.5°	at 755 mm. (31)	$D_4^{69.9}$ = 1.2310 (33)
53.2°	(5) (6) (7)	173.0°	(26) (27)	$n_D^{69.9}$ = 1.52665 (33)
53–54°	(8) (57)	172°	(14) (16) (60)	
53.0–53.1°	(24)	171°	(15)	
53°	(9) (10) (11) (12) (13) (14) (15) (16) (49) (50) (60)	170–171° u.c.	(32)	
52.9°	(17) (18) (19) (20) (21)			
52.84°	(22)			
52.8°	(23)			
52.72°	(25)			
52.70°	(30)			
52.69°	(26)			
52.6°	(27)			
52.52°	(28)			
52.0°	(31)			
52–53°	(29)			

Colorless cryst., alm. insol. aq. (0 077 g. per 1000 g. aq. at 30° (22) cf. (13)); misc. hot alc. (50 ml. abs. alc. + 5 ml. aq. at 25° dis. 4.55 g. C̄ (26)), eas. sol. ether, C_6H_6, $CHCl_3$, CS_2. — Readily sublimes; eas. volatile with steam.

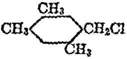
[For data on crystallographic consts. see (34) (35); for data on rate of evapn. of cryst. C̄ see (11); C̄ has molec. f.p. depression of 77 (36) and because of its accessibility, ease of purification, convenient m.p. and large f.p. depression is often used for making mol. wt. detns.]

[For f.p./compn. data and diagram of system *C̄* + *o-dichlorobenzene* (3:6055) (eutectic, m.p. −23.4° contg. 13 3% C̄) see (17) (27); for f.p./compn. data and diagram for system *C̄* + *m-dichlorobenzene* (3:5960) (eutectic, m p. −29.9° contg. 12.0% C̄) see (17); for f.p./compn. data on ternary system of all three dichlorobenzenes see (27). — For f.p./compn. data and diagrams for systems *C̄* + *biphenyl* (1:7175) (eutectic, m.p. 26 9° contg. 57.5 mole % C̄ (6)) (19), *C̄* + *naphthalene* (1:7200) (eutectic, m p. 30.2° contg. 60 6 mole % C̄ (6)), *C̄* + *triphenylmethane* (1:7220) (eutectic, m.p. 35.9° contg. 68.5 mole % C̄ (6)), *C̄* + *nitrobenzene* (eutectic, m.p. −6 8° contg. 32% C̄ (9)), *C̄* + *p-chlorophenol* (3:0475) (eutectic, m.p. 27 2° contg. 26.6 mole % C̄ (18)) see indic. refs. — For thermal anal. of system C̄ + $SbCl_3$ (eutectic, m p. 39 5° contg. 49.5 wt. % C̄ (37)), and of system C̄ + $SbBr_3$ (eutectic, m p. 48.5° contg. 73.5 wt. % C̄ (37)), see (37).]

[C̄ with *p*-dibromobenzene gives a series of solid solns. cf. (38) (39) (40) (41) (23) (24) (26); for study of systems C̄ + *p*-chloro-iodobenzene (23) (34) and C̄ + *p*-di-iodobenzene (23) see indic. refs.]

[For data on densities of solns. of C̄ in C_6H_6 (1:6400) and in *n*-hexane (1:8530) see (42); for data on D_4^{25} and n_α^{25} of solns. of C̄ in C_6H_6 see (7).

3:9702 2,4,5-TRIMETHYLBENZYL CHLORIDE $C_{10}H_{13}Cl$ Beil. V —
(ω-Chlorodurene) V_1—
V_2 - (329)



B.P. 130° at 15 mm. (1)
111–116° at 6 mm. (2)
110° at 5 mm. (2)
98–108° at 1 mm. (3)

[*See also the isomeric* 2,4,6-*trimethylbenzyl chloride* (3:0372).]

[For prepn. of C̄ from 1,2,4-trimethylbenzene (pseudocumene) (1:7470) by chloromethylation with formalin (1:0145) + conc. HCl + HCl gas (yields: 70% (2), 40–43% (3)), or with paraformaldehyde + HCl + $ZnCl_2$ (4), or with chloromethyl methyl ether (3:7085) in AcOH without cat. (yields. 60% (1), 50–60% (5)) (note that some *bis* (chloromethylated) product is also formed) see indic. refs; for prepn. of C̄ from 2,4,5-trimethylbenzyl alc. (see below) with conc. HCl under reflux 5 hrs see (2).]

[C̄ on catalytic hydrogenation presumably yields 1,2,4-trimethylbenzene (pseudocumene) (1:7470) although this particular reaction is not actually reported cf. (1).]

[C̄ on hydrolysis presumably yields 2,4,5-trimethylbenzyl alcohol, cryst from alc., m.p. 83.0–83.5° (2); note, however that this reaction is not actually reported, the alc. having been obtd. by hydrolysis of its acetate, oil, b.p 141–150° at 9 mm. (2).]

C̄ in alc. with aq. NaCN refluxed 5 hrs. gives (85% yield (2)) 2,4,5-trimethylbenzyl cyanide, m p. 9–10°, b.p. 133–147° at 4 mm. (2); note that this nitrile upon hydrolysis with 50% H_2SO_4 at 100° for 2½ hrs. gives 2,4,5-trimethylphenylacetic acid, crude m.p. 116–118° (2), pure m.p 128–129° (2) (corresp. dinitro deriv., m.p. 203–203.5° (2)).

[For condensation of C̄ with ethyl sodio-acetoacetate see (3).]

3:9702 (1) Vavon, Bolle, Calin, *Bull soc chim* (5) 6, 1025–1033 (1939) (2) Smith, MacMullen, *J. Am. Chem Soc.* 58, 633–635 (1936) (3) John, Gunther, *Ber.* 74, 887–888 (1941). (4) Bert, *Comp. rend.* 186, 373–374 (1928) (5) Vavon, Bolle, *Comp. rend* 204, 1826–1828 (1937).

3:9710 *d,l*-3-CHLORO-3-METHYLNONYNE-4 $C_{10}H_{17}Cl$ Beil. S.N. 12

$$CH_3CH_2CH_2CH_2CH_2{\equiv}C{-}\underset{CH_3}{\overset{Cl}{C}}{-}CH_2.CH_3$$

B.P. 82° at 17 mm. (1) $D_4^{20} = 0.8968$ (1) $n_D^{20} = 1.4543$ (1)

[For prepn. of C̄ from 3-methylnonyn-4-ol-3 (1) by saturation with HCl gas (72% yield) see (1).]

[C̄ with MeMgBr gives 73% yield 3,3-dimethylnonyne-4, b.p. 82° at 40 mm, D_4^{20} = 0.7658, n_D^{20} = 1.4313 (1).]

3:9710 (1) Campbell, Eby, *J. Am. Chem. Soc.* 62, 1799–1800 (1940).

3:9712 5-CHLORODECENE-5 $C_{10}H_{19}Cl$ Beil. S.N. 11

$$CH_3CH_2.CH_2CH_2{-}CH{=}\overset{Cl}{C}{-}CH_2.CH_2CH_2CH_3$$

B.P. 99–100° at 28 mm. (1) $D_4^{25} = 0.8753$ (1) $n_D^{25} = 1.4448$ (1)

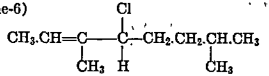
Two geom stereoisomers of C̄ are possible, but only this one has as yet been recognized.

[For prepn. of C̄ from decyne-5 (di-*n*-butylacetylene) [Beil. I_2-(239)] with AcCl + $SnCl_4$

(4-chloro-3-n-butylocten-3-one-2, b.p. 140–146° at 28 mm., $D_4^{25} = 0.9459$, $n_D^{25} = 1.4612$, is also formed (1)) see (1).]

3:9712 (1) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 163–169 (1936).

3:9714 ***d,l*-4-CHLORO-3,7-DIMETHYLOCTENE-2** $C_{10}H_{19}Cl$ **Beil. I —**
(5-Chloro-2,6-dimethyloctene-6) I_1 - (96)
I_2—

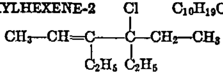


B.P. 83–84° at 12 mm. (1)

[For prepn. of $\bar{C}$ from 2,6-dimethylocten-6-ol-5 [Beil. I-452, I_1-(232)] with 6 N HCl see (1).]

3:9714 (1) Abelmann, *Ber.* **43**, 1583 (1910).

3:9716 4-CHLORO-3,4-DIETHYLHEXENE-2 $C_{10}H_{19}Cl$ **Beil. S.N. 11**

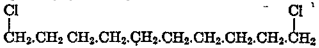


B.P. 70–72° at 10 mm. (1) $D_4^{19} = 0.897$ **(1)** $n_C^{15} = 1.4551$ (1)

For prepn. of $\bar{C}$ from 3,4-diethylhexene-3 (1) with $Cl_2 + NaHCO_3$ at 0° (60% yield accompanied by 40% yield of 3,4-dichloro-3,4-diethylhexane (3:9724)) see (1).]
$\bar{C}$ on treatment with O_3 yields *(1)* acetaldehyde *(1:0100)* q.v.

3:9716 (1) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939).

3:9720 1,10-DICHLORODECANE $C_{10}H_{20}Cl_2$ **Beil. S.N. 10**
(Decamethylene (di)chloride)

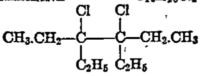


B.P. 147–148° at 11 mm. (1) $D_4^{22} = 0.9941$ **(1)**

[For prepn. of $\bar{C}$ from decanediol-1,10 (decamethylene glycol) (1:5961) by htg. 1 day with excess $SOCl_2$ see (1).]
$\bar{C}$ with NaI in acetone refluxed 4 hrs., acetone evaporated, residual material htd. for 3 hrs. at 140–150° with thiourea in isoamyl alc., yields (1) decamethylene ω,ω'-*bis*-(isothiourea hydrochloride), m.p. 186° (1).

3:9720 (1) Kawai, Hosono, Shikinami, Yonechi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **16**, Nos. 306–309, 9–16 (1931); *Cent.* **1931**, II 1694; *C.A.* **25**, 5665 (1931).

3:9724 3,4-DICHLORO-3,4-DIETHYLHEXANE $C_{10}H_{20}Cl_2$ **Beil. S.N. 10**

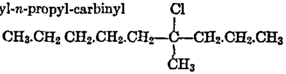


B.P. 101–103 at 10 mm. (1) $D_4^{19} = 1.022$ **(1)** $n_C^{15} = 1.47485$ (1)

[For prepn. of C̄ from 3,4-diethylhexene-3 (1) with $Cl_2 + NaHCO_3$ at 0° (yield 40% accompanied by 60% 4-chloro-3,4-diethylhexene-2 (3:9716)) see (1).]

3:9724 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939).

3:9730 *d,l*-4-CHLORO-4-METHYLNONANE $C_{10}H_{21}Cl$ **Beil. S.N. 10**
(*n*-Amyl-methyl-*n*-propyl-carbinyl chloride)

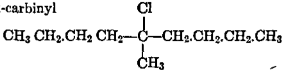


B.P. 43–45° at 1 mm. (1) **D_4^{25} = 0.8663 (1)** **n_D^{25} = 1.4369 (2)**
n_D^{20} = 1.4389 (2)
1.4375 (1)

[For prepn. of C̄ from 4-methylnonanol-4 (*n*-amyl-methyl-*n*-propyl-carbinol) (1) with HCl gas (85% yield (1)) see (1).]

3:9730 (1) Whitmore, Williams, *J. Am. Chem. Soc.* **55**, 408–409 (1933). (2) Smart, Quayle, *J. Am. Chem. Soc.* **67**, 21 (1945).

3:9732 5-CHLORO-5-METHYLNONANE $C_{10}H_{21}Cl$ **Beil. S.N. 10**
(Di-*n*-butyl-methyl-carbinyl chloride)



B.P. 75–77° at 10 mm. (3) **D_4^{25} = 0.8676 (1)**
60.5° at 3.5 mm. (1) **D_4^{20} = 0.8707 (1)** **n_D^{20} = 1.4382 (1)**

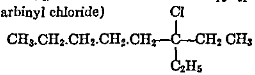
[For prepn. of C̄ from 5-methylnonanol-5 (di-*n*-butyl-methyl-carbinol [Beil. I_1-(213), I_2-(460)] (1) by saturation with dry HCl gas at −10° see (1).]

C̄ on refluxing with 2½ pts. aq. for 9 hrs. gives 14% of its halogen as halide ion (1) (the resultant olefin was not isolated).

[For behavior of C̄ with naphthalene + $AlCl_3$ in CS_2 see (3).]

3:9732 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* **55**, 363–364 (1933). (2) Woodburn, Whitmore, *J. Am. Chem. Soc.* **56**, 1394–1395 (1934). (3) Petrov, Kurbskii, *J. Gen. Chem.* (*U.S.S.R.*) **14**, 492–494 (1944); *C.A.* **39**, 4600 (1945).

3:9734 *d,l*-3-CHLORO-3-ETHYLOCTANE $C_{10}H_{21}Cl$ **Beil. S.N. 10**
(*n*-Amyl-diethyl-carbinyl chloride)



B.P. 42–43° at 0.5 mm. (1) **D_4^{25} = 0.8792 (1)** **n_D^{20} = 1.4423 (1)**

[For prepn. of C̄ from 3-ethyloctanol-3 (*n*-amyl-diethyl-carbinol) [Beil. I-426] (1) with HCl gas (72% yield (1)) see (1).]

3:9734 (1) Whitmore, Williams, *J. Am. Chem. Soc.* **55**, 408–409 (1933).

3:9736 ***d,l*-4-CHLORO-4-ETHYLOCTANE** $C_{10}H_{21}Cl$ Beil. S.N. 10
(*n*-Butyl-ethyl-*n*-propyl-carbinyl chloride)

$$CH_3.CH_2.CH_2.CH_2-\underset{\displaystyle C_2H_5}{\overset{\displaystyle Cl}{C}}-CH_2.CH_2.CH_3$$

B.P. 53–54° at 2 mm. (1) $D_4^{25} = 0.8773$ (1)
$D_4^{20} = 0.8804$ (1) $n_D^{20} = 1.4421$ (1)

[For prepn. of $\bar{C}$ from 4-ethyloctanol-4 (*n*-butyl-ethyl-*n*-propyl-carbinol) [Beil. I_2-(460)] (1) by saturation with dry HCl gas at −10° see (1).]

3:9736 (1) Whitmore, Woodburn, *J. Am. Chem. Soc.* **55**, 363–364 (1933).

3:9738 **3-CHLORO-2,3-DIMETHYLOCTANE** $C_{10}H_{21}Cl$ Beil. S.N. 10
(*n*-Amyl-isopropyl-methyl-carbinyl chloride)

$$CH_3.CH_2.CH_2.CH_2.CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{C}}-\underset{\displaystyle CH_3}{CH}.CH_3$$

B.P. 53–55° at 3 mm. (1) $D_4^{20} = 0.8818$ (1) $n_D^{20} = 1.4420$ (1)

[For prepn. of $\bar{C}$ from 2,3-dimethyloctanol-3 (1) with dry HCl gas at 0° (77% yield) see (1).]

3:9738 (1) Whitmore, Evers, *J. Am. Chem. Soc.* **55**, 813–814 (1933).

3:9740 **8-CHLORO-2,6-DIMETHYLOCTANE** $C_{10}H_{21}Cl$ Beil. I —
(Tetrahydrogeranyl chloride; I_1-(65)
perhydrogeranyl chloride) I_2—

$$\underset{\displaystyle Cl}{CH_2}.CH_2-\underset{\displaystyle CH_3}{CH}-CH_2.CH_2\ CH_2-\underset{\displaystyle CH_3}{CH}-CH_3$$

B.P. 88–89° at 12 mm. (1)
85–86° at 10 mm. (2)

[For prepn. of $\bar{C}$ from 2,6-dimethyloctanol-8 [Beil. I-426, I_1-(214), I_2-(461)] (1) with dry HCl (1) or with PCl_5 (2) see indic. refs.]

[For conversion [illegible] of latter with chloromethyl methyl ether (3:7085) t[illegible] 8-dimethylnonane, b.p. 94–94.5° at 14.5 mm., n_D^{20} = [illegible]

3:9740 (1) Smith, Ungnade, Austin, Prichard, Opie, *J. Org. Chem.* **4**, 338–340 (1939). (2) Ishizaka, *Ber.* **47**, 2454 (1914).

3:9742 **4-CHLORO-4-*n*-PROPYLHEPTANE** $C_{10}H_{21}Cl$ Beil. I —
(Tri-*n*-propylcarbinyl chloride) I_1-(66)
I_2—

$$CH_3\ CH_2\ CH_2-\underset{\displaystyle n\text{-}C_3H_7}{\overset{\displaystyle Cl}{C}}-CH_2.CH_2.CH_3$$

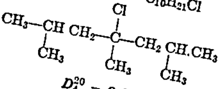
B.P. 80° at 12 mm. (1) $D_4^{20} = 0.8779$ (1) $n_D^{15} = 1.44209$ (1)

[For prepn. of $\bar{C}$ from 4-*n*-propylheptanol-4 [Beil. I-426, I_1-(214), I_2-(461)] by saturation with dry HCl see (1).]

[For data on density and parachor of $\bar{C}$ at 0°, 15°, 25°, 50°, and 75° see (2).]
[For reactn. of $\bar{C}$ with $AlCl_3$ + C_6H_6 yielding 4-phenyl-4-n-propylheptane, b p. 140–141° at 15 mm., D_4^{20} = 0.8694, n_D^{15} = 1.4924, see (1)]

3:9742 (1) Halse, *J. prakt. Chem.* (2) **89**, 459 (1914). (2) Quayle, Owen, Beavers, *J. Am. Chem. Soc.* **61**, 3107–3111 (1939).

3:9744 4-CHLORO-2,4,6-TRIMETHYLHEPTANE $C_{10}H_{21}Cl$
(Di-isobutyl-methyl-carbinyl chloride)



Beil. I —
I_1 - (66)
I_2—

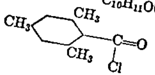
B.P. 82–83° at 25 mm. (1)

D_4^{20} = **0.8657 (1)** n_D^{15} = **1.43336 (1)**

[For prepn. of $\bar{C}$ from 2,4,6-trimethylheptanol-4 (di-isobutyl-methyl-carbinol) [Beil. I-427, I_1-(215)] (1) by saturation with dry HCl gas see (1)]
[For reactn. of $\bar{C}$ with $AlCl_3$ + C_6H_6 to give 4-phenyl-2,4,6-trimethylheptane, b.p. 143–144° at 18 mm., D_4^{20} = 0.8753, n_D^{15} = 1 49497 see (1).]

3:9744 (1) Halse, *J. prakt. Chem.* (2) **89**, 458–459 (1914).

3:9750 2,4,6-TRIMETHYLBENZOYL CHLORIDE $C_{10}H_{11}OCl$
(Mesitoyl chloride;
β-isodurylyl chloride)



Beil. S.N. 943

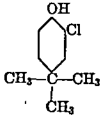
B.P. 143–146°		
118–119°	**at**	**60 mm. (1)**
115.5–116.5°	**at**	**19 mm. (2)**
85.0–85.5°	**at**	**18 mm. (3)**
85.5–86.5°	**at**	**4 mm. (4)**
	at	**2–3 mm. (5)**

D_4^{25} = **1.0967 (3)** n_D^{25} = **1.5263 (3)**

[For prepn of $\bar{C}$ from 2,4,6-trimethylbenzoic acid (mesitoic acid) [Beil IX-553, IX_1-(214)] (1) with $SOCl_2$ (90–97% yield (1)) (2) (3) (5) (6) see indic refs]
[$\bar{C}$ with MeOH yields (3) (4) methyl-2,4,6-trimethylbenzoate (mesitoate) [Beil. IX-553], b p. 212°, 102–103° at 5 5 mm. (3), 101–102° at 3 mm , n_D = 1 4970 (4)]
[$\bar{C}$ with 2,4,6-trimethylphenyl MgBr yields (5) (6) 2,4,6,2′,4′,6′-hexamethylbenzophenone (dimesityl ketone), m.p. 138–139° (5), 136–137° (6); $\bar{C}$ with 2,4,6-trimethylphenacyl MgBr gives (7) 2,4,6,2′,4′,6′-hexamethyldibenzoylmethane (dimesitoylmethane), m p. 96–97° (7)]
$\bar{C}$ on hydrolysis yields (4) 2,4,6-trimethylbenzoic acid, m.p. 152° (amide, m.p 189° (9), 188–188 5° (1), 187–188° (8)).

3:9750 (1) Barnes, *Org. Syntheses* **21**, 77–79 (1941). (2) Murray, Cleveland, Saunders, *J. Am. Chem. Soc.* **63**, 3121 (1941). (3) Kadesch, Weller, *J. Am. Chem. Soc.* **63**, 1311 (1941). (4) Norris, Young, *J. Am Chem. Soc.* **57**, 1424 (1935) (5) Nauta, Wuis, *Rec. trav chim.* **56**, 537–538 (1937). (6) Kohler, Baltzly, *J. Am Chem Soc.* **54**, 4023 (1932). (7) Fuson, Fugate, Fisher, *J. Am. Chem. Soc.* **61**, 2363 (1939). (8) Wheeler, *Am. Chem J.* **23**, 468 (1900). (9) Hantzsch, Lucas, *Ber.* **28**, 748 (1895).

3:9760 2-CHLORO-4-*ter*-BUTYLPHENOL $C_{10}H_{13}OCl$ Beil. S.N. 530-a



B.P. 113–115° at 8 mm. (1)
85–86° at 3–4 mm. (2)
84.5–85° at 3–4 mm. (3)

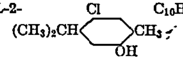
[For prepn. of $\bar{C}$ from *p-ter*-butylphenol (1:1510) by chlorination with *N*-chloroacetamide (cf. (4) (5)) see (1); for other methods see (2) (3).]

[For study of mercuration of $\bar{C}$ see (6).]

Ⓓ 4-*ter*-Butyl-2-chlorophenyl *p*-nitrobenzyl ether: colorless pl. from EtOH, m.p. 90° (1).

3:9760 (1) Jones, *J. Chem. Soc.* **1942**, 678. (2) Mills (to Dow Chem. Co.), U.S. 2,176,010, Oct. 10, 1939; *C. A.* **34**, 858 (1940). (3) Mills (to Dow Chem. Co.), U.S. 2,221,807, Nov. 19, 1940; *C.A.* **35**, 1936 (1941). (4) Orton, King, *J. Chem. Soc.* **99**, 1185–1192 (1911). (5) Orton, Bradfield, *J. Chem. Soc.* **1927**, 993. (6) Moness, Christiansen (to E R. Squibb), U.S. 2,137,236, Nov. 22, 1938; *Cent.* **1939**, I 5007; *C.A.* **33**, 1885–1886 (1939).

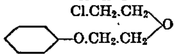
—— **4-CHLORO-5-ISOPROPYL-2-METHYLPHENOL** $C_{10}H_{13}OCl$ Beil. S.N. 531



B.P. 158° at 52 mm. M.P. 42–43°

See 3:0480. *Division A: Solids.*

3:9770 β-CHLOROETHYL-β′-PHENOXYETHYL ETHER $C_{10}H_{13}O_2Cl$ Beil. VI —
[β-(β-Phenoxyethoxy)ethyl chloride] VI₁—
VI₂- (150)



B.P. 149° at 10 mm. (1) $D_{15}^{15} = 1.149$ (1)
138–143° at 8 mm. (2)
113–120° at 1 mm. (3)

[For prepn. (60% yield (1)) from β,β′-dichlorodiethyl ether (3:6025) with alc. $NaOC_6H_5$ (1 mole) see (1).]

[For reaction of $\bar{C}$ in CS_2 or C_6H_6 with $AlCl_3$ + phthalic anhydride, succinic anhydride, maleic anhydride, acetic anhydride see (4).]

[For condensation with amines and phenols see (5); for use as plasticizer see (6).]

3:9770 (1) Cretcher, Koch, Pittenger, *J. Am. Chem. Soc.* **47**, 1174 (1925). (2) Eastman Organic Chemicals, List No. 33 (1942). (3) Bruson (to Röhm and Haas Co.), U.S. 2,249,111, July 15, 1941; *C.A.* **35**, 6698 (1941). (4) Bruson, Es
Röhm and Haas Co., French 824,887, Feb. 1
(6) Murray, Kenyon (to Eastman Kodak Co.
C.A. **28**, 2532 (1934).

3:9780 SEBACYL (DI)CHLORIDE $C_{10}H_{16}O_2Cl_2$ **Beil. II - 719**
II_1-(293)
II_2-(610)

$$\underset{\displaystyle Cl}{O{=}C}{-}(CH_2)_8{-}\underset{\displaystyle Cl}{C{=}O}$$

B.P. 220°	at 75 mm.	(1)	
203°	at 30 mm.	(2)	
182°	at 16 mm.	(3)	
168–170°	at 16 mm.	(4)	
152°	at 15 mm.	(5)	
162–167°	at 11 mm.	(6)	
155–156°	at 8 mm.	(7)	
109–110°	at 1–2 mm.	(11)	

D_4^{20} = **1.1212** (6) $n_D^{18.3}$ = **1.46836** (4)
D_4^{0} = **1.1375** (6)

[For prepn. of $\bar{C}$ from sebacic acid (1:0730) with PCl_5 (90–95% yield (5) (2)) (4), with PCl_3 (3), with $SOCl_2$ (yield: 100% (1), 86% (6), 84% (7)) (8), 83% (11), or with $SiCl_4$ in C_6H_6 + ether (37% yield (9)) see indic. refs.]

$\bar{C}$ with MeOH (1 mole) followed by Na_2CO_3 yields (1) methyl hydrogen sebacate, m p 36° (1); $\bar{C}$ with abs. EtOH (1 mole) yields (7) 9-carbethoxynonanoyl chloride ($C_2H_5OOC.(CH_2)_8.CO.Cl$), b p 158–160° at 7 mm. (7) (corresp 9-carbethoxynonanoic anilide, m.p. 60–61° (7)); $\bar{C}$ with excess phenol yields (8) diphenyl sebacate, m.p. 65–66° (8).

[$\bar{C}$ with $AlCl_3$ + C_6H_6 (1:7400) gives (50% yield (2)) (4) 1,8-dibenzoyloctane, m.p. 91–92° (4), 88–89° (2); $\bar{C}$ with $AlCl_3$ + *m*-xylene (1:7420) gives (10) 1,8-*bis*-(2,4-dimethylbenzoyl)octane.]

[$\bar{C}$ with *n*-$C_6H_{13}MgBr$ gives (28% yield (7)) 10-ketopalmitic acid, m.p. 75–75.8° (7); $\bar{C}$ with *n*-$C_8H_{17}MgBr$ gives (12% yield (7)) 10-ketostearic acid, mp.. 82–82.8° (7); $\bar{C}$ with AgNCO yields (11) sebacyl di-isocyanate.

[$\bar{C}$ in xylene on cat. hydrogenation over $Pd/CaCO_3$ (6) or Pd/diatomaceous earth (5) gives (30–40% yield (5)) corresp. dialdehyde, decandial-1,10 [Beil. I_2-(849)].]

$\bar{C}$ on hydrolysis yields sebacic acid (1:0730); for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to $\bar{C}$ see 1:0730.

3:9780 (1) Meyer, *Monatsh.* **22**, 421 (1901). (2) Auger, *Ann. chim* (6) **22**, 361–364 (1891). (3) Borsche, Wollemann, *Ber.* **44**, 3185–3186 (1911) (4) von Auwers, Schmidt, *Ber.* **46**, 480 (1913). (5) Rosenmund, Zetsche, *Ber* **55**, 609–612 (1922). (6) Waser, *Helv. Chim. Acta* **8**, 124–125 (1925). (7) Fordyce, Johnson, *J. Am Chem. Soc.* **55**, 3369–3370 (1933). (8) Marangoni, *Atti ist. Veneto sci. Pt. 2. Sci. mat. nat.* **97**, 209–218 (1937–1938); *Cent.* **1939**, I 96; *C.A.* **34**, 6934–6935 (1940). (9) Montonna, *J. Am. Chem. Soc.* **49**, 2115 (1927). (10) Borsche, *Ber.* **52**, 2078, 2082 (1919).
(11) Lieser, Macura, *Ann.* **548**, 226–254 (1941); *Cent* **1942**, II 146–148; *C.A.* **37**, 4699 (1942).

3:9792 METHYL ω-(CHLOROFORMYL)PELARGONATE **Beil. S.N. 178**
(ω-(Carbomethoxy)pelargonyl chloride) $C_{11}H_{19}O_3Cl$

$$CH_3OOC{-}(CH_2)_8{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl$$

B.P. 177°	at 23 mm.	(1)
158–160°	at 10 mm.	(2)

Note that $\bar{C}$ is both an acid chloride and an ester.

[For prepn. of $\bar{C}$ from methyl hydrogen sebacate (itself obtd. (52–61% (2)) from sebacic acid (1:0730) + MeOH (1:6120)) by action of $SOCl_2$ (yields: 83–86% (2), 60–70% (1)) see indic. refs]

Ⓓ ω-(Carbomethoxy)pelargonamide (methyl sebacamate): cryst. from aq., m.p. 77.4° (3), 72–74° (2). [From C̄ with conc. aq. NH_4OH at 8° (yields: 93–95% (2), 90% (3)); for dehydration of this prod. (64–71% yield) (3) with P_2O_5 in acetylene tetrachloride to methyl ω-cyanopelargonate, b.p. 170° at 14 mm., $n_D^{25} = 1.4398$ (3), and use of latter in prepn. of high-mol.-wt. linear polymers (4), see indic. refs.]

3:9792 (1) *Morgan, Walton, J. Chem. Soc.* **1936**, 904. (2) *Bishop, Org. Syntheses* **25**, 71–72 (1945). (3) Biggs, Bishop, *J. Am. Chem. Soc.* **63**, 944 (1944). (4) Bishop (to Bell Telephone Laboratories, Inc.), U.S. 2,277,033, March 24, 1942; *C.A.* **36**, 4636 (1942).

3:9800 *n*-UNDECANOYL CHLORIDE $C_{11}H_{21}OCl$ **Beil. S.N. 162**
(*n*-Hendecanoyl chloride)

$$CH_3.(CH_2)_9.\underset{\displaystyle Cl}{\underset{|}{C}}{=}O$$

B.P. 119–120° at 40 mm. (1) $n_D^5 = 1.4465$ (3)
123° at 11 mm. (2)
90° at 1 mm. (3)

Care must be taken to avoid confusion of C̄ with *n*-undecyl chloride (1-chloroundecane) (3:8803).

[For prepn. of C̄ from *n*-undecylic acid (1:0573) with $SOCl_2$ (yield: 95.5% (1)) (3) (4) see indic. refs.]

[C̄ with $C_6H_6 + AlCl_3$ should give *n*-undecyl phenyl ketone, but this compd. is unreported in the literature. — C̄ with toluene (1:7405) + $AlCl_3$ gives (80% yield (5)) *n*-undecyl *p*-tolyl ketone, m.p. 32°, b.p. 196–197° at 12 mm.(?)]

[C̄ with MeOH presumably gives methyl *n*-undecylate [Beil. II_1-(154), II_2-(314)], b.p. 123° at 9–10 mm. (6); similarly, C̄ with EtOH presumably gives ethyl *n*-undecylate [Beil. II-358, II_1-(154)] (known in polymorphic forms for which see (7) (8) (9)); note, however, that prepn. of these esters by this means is not actually reported in the literature).]

[C̄ with phenol presumably gives phenyl *n*-undecylate, but neither this cpd. nor either of the *n*-undecyl hydroxyphenyl ketones to be expected from its rearr. with $AlCl_3$ is reported in the literature. — However, for reaction of C̄ with hydroquinone (1:1590) see (10).]

[C̄ with sodium undecylate on htg. presumably gives undecylic anhydride, m.p. 36.7° (11), 35° (12), but this cpd. is actually reported only by other methods (11) (12).]

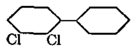
[For reaction of C̄ with diethyl sodioacetosuccinate [Beil. III-801, III_1-(280), III_2-(486)] and subsequent hydrolysis of prod to γ-ketomyristic acid see (4).]

[C̄ with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (2) cf. (13) *N*-(vanillyl)-myristamide, α-form, m.p. 69.5° (2); β-form, m.p. 62.0–62.5° (2); the m.p. of 54–56° reported earlier (13) may have been a mixture, but that of 73–74° by other workers (14) is unexplained.]

C̄ on hydrolysis yields undecylic acid (1:0573), m.p. 29.3°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see undecylic acid (1:0573).

3:9800 (1) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86–89 (1939). (2) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 856 (1934). (3) *Haskelberg, Bergmann, J. Soc. Chem. Ind.* **60**, 166–168 (1941). (4) Robinson, *J. Chem. Soc.* **1930**, 747–748. (5) Hasan, Stedman, *J. Chem. Soc.* **1931**, 2120. (6) Lesser, Weiss, *Ber.* **47**, 2519 (1914). (7) van Bellinghen, *Bull soc. chim. Belg.* **47**, 647, 659, 673, 674, 676, 677, (1938). (8) Mumford, Phillips, *Rec trav. chim.* **52**, 181–194 (1933). (9) Meyer, Reed, *J. Am. Chem. Soc.* **55**, 1582 (1933). (10) Asano, Hase, *J. Pharm. Soc. Japan* **60**, 650–659 (1940); **61**, 1–6 (1941); *C.A.* **36**, 82 (1942).

(11) Wallace, Copenhaver, *J. Am. Chem. Soc.* **63**, 699 (1941). (12) Backer, van der Baan, *Rec. trav. chim.* **56**, 1166 (1937). (13) Nelson, *J. Am. Chem. Soc.* **41**, 2125–2126 (1919). (14) Kobayashi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **6**, 166–184 (1927), *Cent.* **1928**, I 1029.

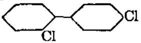
3:9850 2,3-DICHLOROBIPHENYL  $C_{12}H_8Cl_2$ **Beil. S.N. 479**

B.P. 172° at 30 mm. (1)
170–176° at 19 mm. (2)

[For prepn. from 2-amino-3-chlorobiphenyl via diazo reactn see (1); for other methods see (2).]
$\bar{C}$ on oxidn. with CrO_3 + AcOH yields (1) 2,3-dichlorobenzoic acid (3:4650), m.p. 160° (1).

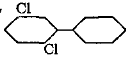
3:9850 (1) de Crauw, *Rec. trav. chim.* **50**, 776–777 (1931) (2) Zerweek, Schutz (to General Aniline and Film Corp), U.S. 2,280,504, April 21, 1942, *C A.* **36**, 5658 (1942).

— 2,4′-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ **Beil. S.N. 479**



B.P. 191° at 30 mm. M.P. 46°

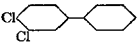
See 3:0670. *Division A: Solids.*

3:9854 2,5-DICHLOROBIPHENYL  $C_{12}H_8Cl_2$ **Beil. V —**
V_1—
V_2-(483)

B.P. 182° at 30 mm. (1)
171° at 15 mm. (2)
147–148° at 8 mm. (3)

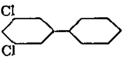
[For prepn of $\bar{C}$ from 2-amino-5-chlorobiphenyl (1) (2), 4,4′-diamino-2,5-dichlorobiphenyl (20% yield (1)), or 2,5-dichloroaniline (3) via appropriate diazo reactions see (1) (2) (3)]
$\bar{C}$ on oxidn. with CrO_3 + AcOH yields (1) (2) 2,5-dichlorobenzoic acid (3:4340), m p. 152° (1), 154° (2).
[For study of reaction of $\bar{C}$ with NaOMe see (4).]

3:9854 (1) de Crauw, *Rec. trav. chim.* **50**, 776–777 (1931). (2) Scarborough, Waters, *J. Chem. Soc.* **1927**, 94 (3) I G., French 851,131, Jan 3, 1940, *C.A* **36**, 1950 (1942). (4) Ref. 1, pp. 784–785, 789.

— 3,4-DICHLOROBIPHENYL  $C_{12}H_8Cl_2$ **Beil. V —**
V_1—
V_2-(483)

B.P. 195–200° at 15 mm. M.P. 46°

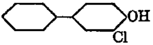
See 3:0685. *Division A · Solids.*

— 3,5-DICHLOROBIPHENYL  $C_{12}H_8Cl_2$ **Beil. V —**
V_1—
V_2-(484)

B.P. 180° at 15 mm. M.P. 36°

See 3:0360. *Division A: Solids.*

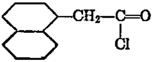
—— 2-CHLORO-4-PHENYLPHENOL $C_{12}H_9OCl$ Beil. S.N. 539



B.P. 176.6° at 5 mm. **M.P. 77°**

See 3:1900. *Division A: Solids.*

3:9856 α-NAPHTHYLACETYL CHLORIDE $C_{12}H_9OCl$ Beil. IX — IX_1-(278)



B.P.	**188°**	at 23 mm.	(1)
	180°	at 17 mm.	(7)
	174°	at 15 mm.	(2)
	148–155°	at 0.5 mm.	(3)

[For prepn. of C̄ from α-naphthylacetic acid (1:0728) with PCl_5 (4) (1), or with $SOCl_2$ alone (2) (5) or in C_6H_6 (6), see indic. refs.]

C̄ with $AlCl_3$ in nitrobenzene (1) (but *not* by $SnCl_4$ in CS_2 at room temp. (2)) losses HCl and ring-closes yielding acenaphthenone (1:5200), m.p. 121° cor.

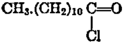
[C̄ with aminoacetic acid (glycine) yields (5) *N*-(α-naphthylacetyl) glycine, m p. 153–154° (5). (For reactn. of C̄ with other amino acids and use as plant hormone see (5)).]

C̄ on hydrolysis yields α-naphthylacetic acid (1:0728) q.v. for the corresp. amide and anilide.

3:9856 (1) Badische Anilin- und Soda-Fabrik, Ger. 230,237, Jan. 20, 1910; *Cent.* **1911,** I 358. (2) Cook, Hewett, *J. Chem. Soc.* **1933,** 1106. (3) Wolfram, Schörnig, Hausdörfer (to I.G.), Ger. 562,391, Nov. 1, 1932; *Cent.* **1933,** I 849. (4) Boessneck, *Ber.* **16,** 641 (1883). (5) Isler (to Hoffmann-LaRoche Inc.), U.S. 2,179,979, Nov. 14, 1939; *C.A.* **34,** 1808 (1940); Brit. 510,138, July 27, 1939; *Cent.* **1939,** II 3872; *C.A.* **34,** 4080 (1940); Swiss 203,078, May 16, 1939; *Cent.* **1939,** II 3872. (6) Gilman, Kirby, *J. Am. Chem. Soc.* **51,** 3477, Note 18 (1929). (7) King, Henshall, *J. Chem. Soc.* **1945,** 418.

3:9858 *n*-DODECANOYL CHLORIDE $C_{12}H_{23}OCl$ Beil. II - 363 II_1-(159) II_2-(321)

(*n*-Lauroyl chloride)



M.P. − 17° (6) n_D^{20} = **1.4458** (7)

B.P.	**175–176°**	at 47 mm.	(1)
	150°	at 22 mm.	(2)
	145–147°	at 20 mm.	(3)
	145°	at 18 mm.	(4)
	146–150°	at 17 mm.	(20)
	143–148°	at 15 mm.	(5)
	142.5°	at 15 mm.	(6)
	140°	at 15 mm.	(7)
	141°	at 14 mm.	(8)
	134–137°	at 11 mm.	(9)
	135–140°	at 10 mm.	(10)
	134–137°	at 11 mm.	(11)
	132°	at 9 mm.	(12)

$\bar{C}$ is widely used as anti-moth agent and vapor fumigant but lit. and patents are so numerous that they cannot be included here; note, however, prevention of caking of $\bar{C}$ by mixt. with 1–10% paraformaldehyde (43). — [For study of toxicity of $\bar{C}$ see (44). — For use of $\bar{C}$ in prepn. of sulfur dyes see (45).]

[For detn. of $\bar{C}$ in air see (46); for detn. of $\bar{C}$ in soil by means of detn. of refractive index of solns. in kerosene see (47).]

[For prepn. of $\bar{C}$ from *p*-chloroaniline [Beil. XII-607, XII_1-(304)] via diazotization, prepn. of diazonium/$ZnCl_2$ double salt, and decompn. of latter in molten phenol (41% yield $\bar{C}$ together with 31% hydroxybiphenyl + 15% diphenyl ether) see (48); from *p*-phenylenediamine [Beil. XIII-61, $XIII_1$-(18)] via tetrazotization in AcOH (49) or H_3PO_4 (50) with nitrosylsulfuric acid followed by subsequent reactn. with Cu_2Cl_2 (yield: 70% (49) (50)) cf. (51), or by reduction with $SnCl_2$/HCl to *p*-phenylenedihydrazine and oxidn. with $CuSO_4$ (52), see indic. refs.]

[For prepn. of $\bar{C}$ from *p*-chloro-nitrobenzene [Beil. V-243, V_1-(130)] with conc. HCl in s.t. at 270° (53), or with $SOCl_2$ in s.t. at 160–200° (54) (55), see indic. refs.; from *p*-bromonitrobenzene [Beil. V-248, V_1-(132)] (56), phenol-*p*-sulfonic acid [Beil. XI-241, XI_1-(55)] (57), or *p*-chlorophenol (3:0475) (16) with PCl_5 on htg. see indic. refs; from *p*-chlorobenzenesulfonic acid [Beil. XI-54, XI_1-(14)] with $SOCl_2$ in s.t. at 160–200° see (54) (55); from 2,5-dichlorobenzophenone (3:2340) by fusion with KOH/NaOH (65% yield) see (58); from di-*p*-chlorophenyl sulfide or di-*p*-chlorophenyl sulfoxide with S at 260–270° for 3–8 hrs. see (59); from *p*-chlorophenyl selenium trichloride by htg. at 184° (90% yield) see (12).]

[For formn. of $\bar{C}$ (together with *o*- and *m*-isomers in some cases) from C_6H_6 with Cl_2 in pres. of I_2 (15), $MoCl_5$ (60), $AlCl_3$ (61), or conc. H_2SO_4 (62), by electrolysis of susp. in AcOH + aq. HCl (69) or with aqua regia (70), see indic. refs.; from chlorobenzene (3:7903) with Cl_2 + cat. at 600° (17) cf. (63), or with Cl_2 in pres. of $AlCl_3$ (65% yield (27)), $FeCl_3$ (55% yield (27)), or Al/Hg (66), see indic. refs; from chlorobenzene (3:7903) with $Al_2S_2Cl_8$ (i.e., $2AlCl_3 + S_2Cl_2$ (64)) + SO_2Cl_2 (64) (65), or by boilg. with $FeCl_3$ (67), or in small amt. by htg. with $PbCl_4 \cdot 2NH_4Cl$ in s.t. at 210° (68), see indic. refs.]

[$\bar{C}$ with Cl_2 (61) in pres. of Al/Hg (66) or $\bar{C}$ with $Al_2S_2Cl_8$ (i.e., $2AlCl_3 + S_2Cl_2$) + SO_2Cl_2 (64) gives (58% yield (64)) 1,2,4-trichlorobenzene (3:6420); $\bar{C}$, however, chlorinates *less* readily than *o*-dichlorobenzene (3:6055), and if their mixture or eutectic is chlorinated residual $\bar{C}$ can be separated by fractional freezing (71) (72) (73). — $\bar{C}$ with Cl_2 in pres. of Fe (74) or with $Al_2S_2Cl_8$ (i.e., $2AlCl_3 + S_2Cl_2$) + SO_2Cl_2 as directed (64) gives (yields: 67% (64), 39% (74)) (75) 1,2,4,5-tetrachlorobenzene (3:4115). — $\bar{C}$ with liq. Cl_2 + sunlight + cat. (76) (77) or $\bar{C}$ in CCl_4 under 1% aq. NaOH in sunlight (76) adds $3Cl_2$ yielding a mixt. of β- (m.p. 262° (76)) and α- (m.p. 89.6° (76)) *p*-dichlorobenzene hexachlorides (use as insecticide (77)). — For study of photochem. chlorination of $\bar{C}$ see (78).]

[$\bar{C}$ when pure can be recovered unchanged after boiling with liq. Br_2 (79); however, $\bar{C}$ warmed with Br_2 in pres. of Fe (79) or htd. with Br_2 + $NaNO_2$ + fumg. H_2SO_4 in s.t. at 200° for 4 hrs. (80) gives (19% yield (79)) 2,5-dibromo-1,4-dichlorobenzene, ndls. from hot alc., m.p. 148° (79), 146° (80). — $\bar{C}$ with excess Br_2 + $AlCl_3$ as directed (81) gives 2,3,5,6-tetrabromo-1,4-dichlorobenzene, m.p. 278–278.5° (81).]

[$\bar{C}$ passed over Pt spiral at bright red heat yields (82) 2,5,2',5'-tetrachlorobiphenyl, m.p. 84–85° (82). — $\bar{C}$ in EtOH at 55° in pres. of Adams' cat. (PtO_2) with excess H_2 at 3 atm. press. yields (83) cyclohexane (1:8405). — $\bar{C}$ in alc. KCN with $NiCl_2$ htd. in s.t. 20 hrs. at 260–270° gives (12% yield (84)) terephthalic acid (1:0910).]

[$\bar{C}$ with Na + *n*-butyl chloride (3:7160) in xylene at 150° gives small yield (85) *p*-di-*n*-butylbenzene, b.p. 224–225.5° at 759 mm. (85). — $\bar{C}$ with Mg + I_2 (0.25 equiv.) gives in 6 hrs. 58% yield (86) *p*-chlorophenyl MgCl.]

C̄ has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. C̄ on htg. with phenols splits out HCl yielding the corresp. esters. [E g, *C̄ with phenol (1:1420) gives (6) phenyl laurate, m.p. 24.5° (6), b.p. 210° at 15 mm. (6),* 159–161° at 1 mm. (35); C̄ with *p*-cresol (1:1410) gives (6) *p*-tolyl laurate, m p. 28° (6), b.p. 219.5° at 15 mm. (6). — C̄ (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (36) pyrocatechol dilaurate, m.p. 35.5°; C̄ (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (36) resorcinol dilaurate, m.p. 43–44.5°; C̄ (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (36) hydroquinone dilaurate, m.p. 85–86°.]

[C̄ with phenol (1:1420) + $AlCl_3$ in *sym.*-tetrachloroethane (3:5750) as solvent, however, gives (37) (35) (38) a mixt. of the corresp. hydroxylaurophenones; viz., 32 6% yield (37) *o*-hydroxyphenyl undecyl ketone, m.p. 44–45.5° (corresp. 2,4-dinitrophenylhydrazone, m.p. 92–93°) and 24.6% yield (37) *p*-hydroxyphenyl undecyl ketone, m.p. 71–72° (corresp. 2,4-dinitrophenylhydrazone, m.p. 150–151°); for study of influence upon *o*/*p* ratio of use of nitrobenzene and CS_2 as solvents see (38); for prepn. of these hydroxylaurophenones from phenyl laurate by BF_3 rearr. see (39); for their methyl ethers see (44).]

With salts of organic acids. [C̄ with Na laurate at 100° with protection from moist air gives (40) lauric anhydride (1:0601), m.p. 44° (41), 42.1° (42), 41.8° (43), 41° (40), but the latter is usually prepd. from lauric acid (1:0605) by htg. with Ac_2O (41) (42) (43)]

With Grignard reagents. C̄ with RMgX reagents derived from tertiary halides not only undergoes the normal reaction to give the corresp. secondary alcohol but also suffers reduction [e.g., C̄ with *ter*-BuMgCl gives (7) the expected 2,2-dimethyltetradecanol-3 (67% yield) together with lauryl alc. (1:5900) (13.7%) and *ter*-butyl-undecyl-carbinyl laurate (10.4%); similarly, C̄ with *ter*-AmMgCl gives (7) lauryl alc. (1:5900) (54.8%) *and 3,3-dimethylpentadecanol-4 (17.7%)].*

With organic amines. C̄ with organic pr [illegible] C̄ with *p*-cymidine (2-methyl-5-isopropylar [illegible] anilide, m.p. 82–83°; C̄ with vanillylamine [illegible] *N*-(vanillyl)lauramide, *α*-form, m.p. 72.5–73°, *β*-form, m.p. 67–67.5°].

C̄ on hydrolysis yields lauric acid (1:0605), m p. 43–44°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see lauric acid (1:0605).

3:9858 (1) Hann, Jamieson, *J. Am. Chem. Soc.* **50**, 1443 (1928). (2) Averill, Roche, King, *J. Am. Chem. Soc.* **51**, 868 (1929). (3) Adams, Ulich, *J. Am. Chem. Soc.* **42**, 604 (1920). (4) Caspari, *Am. Chem. J.* **27**, 305 (1902). (5) Gault, Ehrmann, *Bull. soc. chim.* (4) **39**, 875–876 (1926). (6) Krafft, Burge [illegible] **17**, [illegible] *Soc.* **63**, *649–650 (1941).* [illegible] *Helv. Chim. Acta* [illegible] (11) Ju, Shen, [illegible] *Rec. trav. chim.* [illegible] (1933). (14) Darzens, Mentzer, *Compt. rend.* **213**, 268–271 (1941). (15) Ralston, McCorkle, Vander Wal (to Armour and Co), U.S. 2,262,431, Nov. 11, 1941; *C.A.* **36**, 1513 (1942). (16) Tilak, Venkataraman, *J. Sci Ind. Research (India)* **3**, 193–197 (1944); *C.A.* **39**, 4242 (1945). (17) Izard, *Biochem Z* **40**, 401 (19[illegible] **11**, 30–34 (1914); *C.A.* **38**, 6274 (1944). (19) Soc. d [illegible], 1931; *Cent.* **1931**, II 1350; *C.A.* **25**, 1575 [illegible]; *C.A.* **24**, 5767 (1930): Brit. 330,511, J[illegible] (20) [illegible] *Cent.* **1929**, II [illegible] 3, 1936; *Cent.* [illegible] (1944). (24) [illegible] (1912). (26) Haller, Bauer, *Compt. rend.* **149**, 7 (1909). (27) I.G , Brit. 453,778, Oct 15, 1936; *Cent* **1937**, I 727; *C.A.* **31**, 1122 (1937). (28) Sabatier, Mailhe, *Compt. rend* **158**, 834 (1914). (29) I.G., French 801,499, Aug. 5, 1936; *Cent.* **1937**, I 1016; *C.A.* **31**, 483 (1937). (30) Ralston, Christensen, *Ind. Eng. Chem.* **29**, 194–196 (1937).

Note that care must be taken to avoid confusion of $\bar{C}$ with n-lauryl chloride (1-chlorododecane) (3:8810).

PREPARATION OF $\bar{C}$

[For prepn. of $\bar{C}$ from n-lauric acid (1:0605) with PCl_5 (yields: 91.5% (10), 66% (13)) (6) (15) (32), with $PCl_5 + ZnCl_2$ (45% yield (13)), with PCl_3 (yields: 80% (8), 72% (13)) (4) (16), with $PCl_3 + ZnCl_2$ (79% yield (13)), with $SOCl_2$ (yields: 92% (9), 80–84% (11), 83% (13), 80% (20)) (1) (5) (17) (32) (33), with oxalyl (di)chloride (3:5060) (99% yield (3)) (2), or with carbonyl chloride (phosgene) (3:5000) at 140–150° (85–90% yield (18)) see indic. refs.]

[For prepn. of $\bar{C}$ from α,β-dichloroethyl laurate (19) on distn. with 0.1% $ZnCl_2$ (chloroacetaldehyde (3:7212) is also formed) see (19).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Behavior with Inorganic Reactants

Hydrogenation of $\bar{C}$. [$\bar{C}$ with H_2 + Pt cat. at 200–320° and 50–180 mm. or with H_2 + Raney Ni at 160° and 50 mm. *fails* (8) to give the expected lauraldehyde (1:0017); this result is apparently due to side reactions of the latter since undecane (1:8820) and tricosane, $C_{23}H_{48}$, were isolated (8).]

Behavior with sodium. [$\bar{C}$ (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 4 hrs. gives (60% yield (20)) tetracosen-12-diol-12,13 dilaurate, i e., the dilaurate ester of $CH_3.(CH_2)_{10}.C(OH){=}C(OH)\,(CH_2)_{10}.CH_3$, cryst. from acetone/$C_6H_6$ (3:1), m.p. 42–43° (20)]

Behavior with Na_2O_2. [$\bar{C}$ with aq. Na_2O_2 below 50° gives (21) dilauroyl peroxide, but no constants for either this prod. or for lauroyl hydrogen peroxide can be found in the literature; for use of dilauroyl peroxide as cat. for drying oils see (22).]

Behavior with NaN_3. [*$\bar{C}$ with NaN_3 in C_6H_6 reacts to give lauroyl azide (not isolated* (23)), which loses N_2 and rearr. giving (81–86% yield (23)) undecyl isocyanate, b p. 103° at 3 mm. (23).]

Behavior with Organic Reactants

With hydrocarbons. [$\bar{C}$ with $C_6H_6 + AlCl_3$ gives (yields· 100% (14), 71% (11)) (24) (25) (26) (27) phenyl undecyl ketone (laurophenone) [Beil. VII-345, VII₁-(186)], m p. 47° (24) (28), 46° (14) (25), 45° (26), 44–45° (11); b.p. 222–223° at 21 mm. (25), 201–202° at 9 mm. (26), 193–194° at 9 mm. (11), 174° at 3 mm. (29) (corresp. oxime, m.p. 64.5° (11); semicarbazone, m.p. 98° (11); 2,4-dinitrophenylhydrazone, m.p. 101–102° (11)). — For analogous reactions of $\bar{C}$ in pres. of $AlCl_3$ with biphenyl (1:7175), diphenyl ether (1:7125), diphenylene oxide (1:7205), carbazole, thiophene, and furan see (30); for use of these products as waxes, addition agents for lubricants, etc., see (30) (31).]

With alcohols. $\bar{C}$ with alcohols gives in general the corresp. alkyl laurates [e g., $\bar{C}$ with MeOH gives methyl laurate, m p. +5°, b.p 148° at 18 mm. (10); $\bar{C}$ with EtOH gives ethyl laurate (1:4196), m p. −1.7 b p. 269°; etc. — $\bar{C}$ with benzyl alc. (1:6480) gives (32) benzyl laurate; $\bar{C}$ with menthol (1:5940) gives (33) menthyl laurate; etc.].

$\bar{C}$ (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., $\bar{C}$ with ethylene glycol (1:6465) gives (34) ethylene glycol dilaurate (1:2157), m p. 52°; $\bar{C}$ with propanediol-1,2 (1:6455) gives (34) propylene glycol dilaurate, m p 35°; $\bar{C}$ with butanediol-1,3 (1:6482) gives (34) 1,3-butylene glycol dilaurate, m p. about 16.5°; $\bar{C}$ with butanediol-1,4 (1:6516) gives (34) tetramethylene glycol dilaurate, m.p. 45.5°].

[For prepn. of C̄ from *m*-chlorobromobenzene [Beil. V-209, V_1-(115), V_2-(161)] (2) by conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *o*-chlorobenzonitrile [Beil. IX-336] (4) (5) followed by hydrolysis (73% yield) see (1).]

Ⓓ **2,3′-Dichlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 255–257° (1).

3:9859-A (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1601–1602 (1945). (2) Hartwell, *Org. Syntheses* **24**, 22–24, Note 5 (1944). (3) Hein, Retter, *Ber.* **71**, 1968 (1938). (4) Norris, Klemka, *J. Am. Chem. Soc.* **62**, 1433 (1940). (5) Baudet, *Rec. trav. chem.* **43**, 707–708 (1924).

3:9860 TRIDECANOYL CHLORIDE $C_{13}H_{25}OCl$ Beil. S.N. 162

$$CH_3\,(CH_2)_{11}\text{—}\underset{\displaystyle Cl}{\underset{|}{C}}\text{=}O$$

B.P. 145–146° at 11 mm. (1)
145–147° at 10 mm. (2)
144–145° at 10 mm. (3)

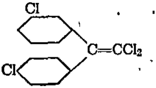
[For prepn. of C̄ from tridecanoic acid (1:0600) with $SOCl_2$ (3) (96.5% yield (2)) see indic. refs.]

[For reactn. of C̄ with $C_6H_6 + AlCl_3$ yielding phenyl *n*-dodecyl ketone, m.p. 41–42°, b.p. 170° at 0.1 mm. (semicarbazone, m.p. 101°), see (3); for reactn. of C̄ with vanillylamine see (1); for reactn. of C̄ with 1,7-aminonaphthol see (4).]

C̄ on hydrolysis yields tridecanoic acid (1:0600) (for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see 1:0600).

3:9860 (1) Ford-Moore, Phillips, *Rec. trav. chim* **53**, 856–857 (1934). (2) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86–89, 101 (1939). (3) Ziegler, Dersch, Wollthan, *Ann.* **511**, 38–39 (1934).

3:9863 1,1-DICHLORO-2-(*m*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHYLENE $C_{14}H_8Cl_4$ Beil. S.N. 480



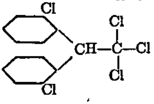
B.P. 158–162° at 1 mm. (1)

[For prepn. of C̄ from "*m,p*-DDT" (3:9867) by elimination of 1 HCl with alc. KOH (80% yield) see (1).]

C̄ on oxidn. with CrO_3 gives (41% yield (1)) 3,4′-dichlorobenzophenone (3:3415), m.p. 113°.

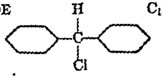
3:9863 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

3:9865 1,1,1-TRICHLORO-2,2-*bis*-(*o*-CHLOROPHENYL)ETHANE ("*o,o′*-DDT") $C_{14}H_9Cl_5$ Beil. S.N. 479



... Co.), U.S. 2,033,544, March 10, 1936; *Cent* 1936, ... Row, *J. Am. Chem. Soc.* 43, 363 (1921). (33) ...) Staudinger, Schwalenstöcker, *Ber.* 68, 725–742 ... *Chem.* 5, 658 (1940). (36) Marangoni, *Atti* ... (1937/8); *Cent.* 1939, I 95–96; *C.A.* 34, 6934 (1940). (37) Ralston, Bauer, *J. Org. Chem.* 5, 165–170 (1940). (38) Ralston, Ingle, McCorkle, *J. Org. Chem.* 7, 457–461 (1942). (39) Balle, Heimke (to I.G.), Ger. 637,808, Nov. 4, 1936; ...

—— **BENZOHYDRYL CHLORIDE** $C_{13}H_{11}Cl$ **Beil. V - 590**
V_1-(278)
V_2-(500)



B.P. 190–191° at 247 mm. **M.P. 18°** **$D_4^{19.5} = 1.1398$** **$n_D^{19.5} = 1.5959$**

See 3:0060. *Division A: Solids.*

3:9859 1-CHLOROTRIDECANE $CH_3.(CH_2)_{11}.CH_2Cl$ $C_{13}H_{27}Cl$ **Beil. S.N. 10**
(*n*-Tridecyl chloride)

B.P. 135.7–136.0° at 9 mm. (1) **$D_4^{20} = 0.8668$ (1)** **$n_D^{20} = 1.4460$ (1)**

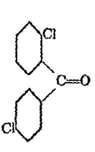
[For prepn. of $\bar{C}$ from *N*-benzoyl-*n*-tridecylamine (*N*-(*n*-tridecyl)benzamide) with PCl_5 at 160–210° (67% yield) see (1).]

$\bar{C}$ with Mg in dry ether gives n-$C_{13}H_{27}MgCl$ (1) [this prod. with allyl bromide as directed gives (48% *yield* (1)) *hexadecene-1 (cetene) (1.7000)*].

——*n*-Tridecyl *p*-nitrobenzoate: m.p. 37.4° cor. (2). [Prepd. indirectly (2).]
——*n*-Tridecyl 3,5-dinitrobenzoate: unreported
——*N*-(*n*-Tridecyl)phthalimide: unreported

3:9859 (1) Suida, Drahowzal, *Ber.* 75, 996 (1942). (2) Armstrong, Copenhaver, *J. Am. Chem. Soc.* 65, 2252–2253 (1943).

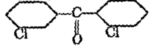
—— **2,4′-DICHLOROBENZOPHENONE** $C_{13}H_8OCl_2$ **Beil. VII - 420**
VII_1—



B.P. 214–215° at 22 mm. **M.P. 66–67°**

See 3:1565. *Division A: Solids.*

3:9859-A 2,3′-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ **Beil. S.N. 652**
(*o*-Chlorophenyl *m*-chlorophenyl ketone)



B.P. 140–142° at 1 mm. (1)

Oil, which on attempted distillation dec. (1) (2) into HCl + 1,2-diphenylethylene (stilbene) (1:7250). — $\bar{C}$ can, however, be distilled with steam (1).

[For prepn. of $\bar{C}$ from C_6H_6 with chloroacetaldehyde (3:7212) (generated in mixt. by use of α,β-dichloroethyl ethyl ether (3:5640)) + conc. H_2SO_4 see (2); for formn. in very small amt. from 1,1,1-trichloro-2,2-diphenylethane [Beil. VI-606, VI_1-(285)] during electrolytic reduction in alc./HCl see (3).]

$\bar{C}$ with alc. KOH loses HCl yielding (1) 1,1-diphenylethylene [Beil. V-639, V_1-(308), V_2-(543)], b.p. 277°, accompanied by its polymers.

3:9871 (1) Hepp, *Ber.* **7**, 1409–1413 (1874). (2) Hepp, *Ber.* **6**, 1439 (1873). (3) Brand, *Z. Elektrochem.* **16**, 670 (1910).

3:9874 1-CHLOROTETRADECANE $C_{14}H_{29}Cl$ Beil. I —
(*n*-Tetradecyl chloride; $CH_3.(CH_2)_{12}\,CH_2Cl$ I_1—
n-myristyl chloride) I_2-(135)

B.P. 154–155° at 15 mm. (1) D_4^{20} **= 0.8589 (2)** n_D^{20} **= 1.4450 (2)**
139–142° at 4 mm. (2)
44–53° at 2 × 10^{-4} mm. (2)

Care must be taken to avoid confusion of $\bar{C}$ with the acid chloride of *n*-tetradecanoic acid (myristic acid), commonly designated as *n*-myristoyl chloride (3:9885).

[For prepn. of $\bar{C}$ from tetradecanol-1 (1:5935) with conc. HCl + $ZnCl_2$ or by htg. in s.t. with fumg. HCl see (1); for formn of $\bar{C}$ (31% yield) from tetradecanol-1 (1:5935) with PCl_3 in pres. of mesityl oxide and Ac_2O see (2).]

[$\bar{C}$ (1 mole) with pyridine (1 mole) in s.t. at 110° for 15 hrs. gives (3) the corresp. quaternary salt, viz., *N*-(*n*-tetradecyl)pyridinium chloride, cryst. from alc./ether or from C_6H_6 as monohydrate, m p. 85.5° (3), 75 5° (5) (this prod. on cat. hydrogenation gives (3) *N*-(*n*-tetradecyl)piperidinium hydrochloride, m.p. 186–187° (3). — For analogous reactn. of $\bar{C}$ with isoquinoline see (3)]

[For study of rate of reactn. of $\bar{C}$ with KI in acetone at 50° and 60° see (1).]

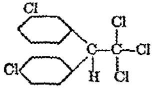
—— *n*-Tetradecyl *p*-nitrobenzoate: m p. 51 2° cor. (4). [Prepd. indirectly.]
—— *n*-Tetradecyl 3,5-dinitrobenzoate: unreported.
—— *N*-(*n*-Tetradecyl)phthalimide: unreported.
—— *S*-(*n*-Tetradecyl)isothiourea picrate: unreported.
—— *n*-Tetradecyl mercuric chloride: unreported (but see (6)).

3:9874 (1) Conant, Hussey, *J Am. Chem. Soc.* **47**, 483, 485 (1925). (2) Drake, Marvel, *J. Org. Chem.* **2**, 394 (1937). (3) Karrer, Kahnt, Epstein, Jaffé, Ishii, *Helv. Chim. Acta* **21**, 233–234 (1938). (4) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252–2253 (1943). (5) Lottermoser, Froscher, *Kolloid-Beihefte* **45**, 305–306, 315, 319, 323, 339 (1937). (6) Meals, *J. Org. Chem* **9**, 215 (1944).

This compound is the so-called *o,o'*-isomer of "DDT" (3:3298). Although it is known to be a contaminant of "DDT" (e.g., 6% (1)) no accurate information regarding it is at present available.

3:9865 (1) Gunther, *J. Chem. Education* 22, 239 (1945).

3:9867 1,1,1-TRICHLORO-2-(*m*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHANE $C_{14}H_9Cl_5$ **Beil. S.N. 479**
("*m,p'*-DDT")



B.P. 181–185° at 1 mm. (1)

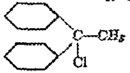
[For prepn. of $\bar{C}$ from 2,2,2-trichloro-1-(*m*-chlorophenyl)ethanol (1) by condensation with chlorobenzene (3:7903) in presence of fumg. H_2SO_4 (48% yield) see (1).]

[$\bar{C}$ with alc. KOH loses HCl giving (80% yield (1)) 1,1-dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:9863).]

$\bar{C}$ on dinitration with equal wt. fumg HNO_3 gives (90% yield (1)) a dinitro cpd., m.p. 118.8–120.1° (1).

3:9867 (1) Haller, Bartlett, Drake, Newman, Cristol, *J. Am. Chem Soc.* 67, 1600 (1945).

3:9870 1,1-DIPHENYLETHYL CHLORIDE $C_{14}H_{13}Cl$ **Beil. S.N. 479**
(Chloro-diphenyl-methyl-methane)



[*See also* 2,2-*diphenylethyl chloride* (3:9871).]

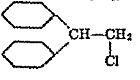
$\bar{C}$ cannot be obtd. in cryst form; at room temp. $\bar{C}$ slowly dec. (1) to give HCl and 1,1-diphenylethylene [Beil V-639, V_1-(308), V_2-(543)], b p. 277°, accompanied (1) (3) by a small amt. of 1,1,3,3-tetraphenylbutene-1, m p. 113–114° (the unsatd. dimer of 1,1-diphenylethylene).

[For prepn. of $\bar{C}$ from diphenyl-methyl-carbinol [Beil. VI-685, VI_1-(330)] in C_6H_6 (1) or pet. ether (2) in pres. of $CaCl_2$ by saturation at 0–10° with dry HCl gas and stdg overnight see indic. refs.]

$\bar{C}$ in C_6H_6 stood at room temp. gives (95–97% yield in 1 week, 80% in 1 day (1)) 1,1,3-triphenyl-3-methylhydrindene (the saturated dimer of 1,1-diphenylethylene), colorless cryst. from alc, m p. 143° (1); note that attempts to accelerate this reaction by warming give decreased yield together with formation of 1,1-diphenylethylene and its unsaturated dimer (mentioned above).

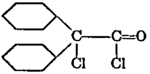
3:9870 (1) Schoepfle, Ryan, *J. Am Chem. Soc.* 52, 4025–4027 (1930). (2) Schoepfle, Ryan, *J. Am. Chem. Soc.* 54, 3692 (1932). (3) Blicke, Powers. *J. Am. Chem Soc* 52, 3383 (1929).

3:9871 2,2-DIPHENYLETHYL CHLORIDE $C_{14}H_{13}Cl$ **Beil. V - 606**
V_1-(285)
V_2—



[*See also* 1,1-*diphenylethyl chloride* (3:9870).]

—— α-CHLORO-DIPHENYLACETYL CHLORIDE $C_{14}H_{10}OCl_2$ Beil. IX - 675
IX$_1$-(283)



B.P. 180° at 14 mm. **M.P. 50°**

See 3:0885. *Division A: Solids.*

3:9885 *n*-TETRADECANOYL CHLORIDE $C_{14}H_{27}OCl$ Beil. II - 368
(*n*-Myristoyl chloride) $CH_3(CH_2)_{12}.C(=O)Cl$ II$_1$-(162)
II$_2$-(329)

B.P.	**195°**	at 45–47 mm.	(1)	**M.P. −1°** (7)
	179–180°	at 22 mm.	(2)	
	175–176°	at 16–17 mm.	(3)	
	174°	at 16 mm.	(4)	
	169°	at 15 mm.	(5)	
	168°	at 15 mm.	(6) (7)	
	160–162°	at 11 mm.	(8)	
	159–161°	at 11 mm.	(9)	
	134°	at 2.5 mm.	(10)	
	119.5–123°	at 1 mm.	(11)	

Care must be taken to avoid confusion of C̄ with *n*-myristyl chloride (1-chlorotetradecane) (3:9874).

PREPARATION OF C̄

[For prepn. of C̄ from myristic acid (1:0630) with $SOCl_2$ (yields: 91% (8), 80% (3), 80–84% (9), 79% (6)) (12) (2) (13) (14) (15); with PCl_5 (89% yield (6)) (7) (14); with PCl_3 (11) (1) (17); with $PCl_3 + ZnCl_2$ (79% yield (6)); or with oxalyl (di)chloride (3:5060) (10) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Behavior with Inorganic Reactants

Hydrogenation of C̄. [C̄ with H_2 + Pt cat. at 220–230° at 60–65 mm. gives (1) not only some *n*-myristaldehyde (1:0004) and its trimer but also (by loss of CO from C̄) *n*-tridecane [Beil. 1-171, I$_2$-(134)], b.p. 234°.]

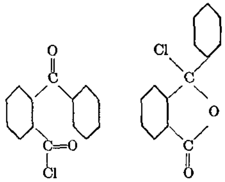
Hydrolysis of C̄. C̄ on hydrolysis with aq. presumably yields myristic acid (1:0630) + HCl although actual record of this reaction is lacking in the literature.

Behavior with sodium. [C̄ (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed (with stirring) for 10 hrs. gives (64% yield (3)) octacosen-14-diol-14,15 dimyristate, i.e., the dimyristate ester of $CH_3.(CH_2)_{12}.C(OH){=}C(OH).(CH_2)_{12}.CH_3$, cryst. from acetone/$C_6H_6$ (3:1), m.p 54–55° (3).]

Behavior with Organic Reactants

With hydrocarbons (or their equivalents). [C̄ with $C_6H_6 + AlCl_3$ in CS_2 gives (69% yield (9)) phenyl *n*-tridecyl ketone (myristophenone) [Beil. VII$_1$-(186)], m.p. 52–53°

3:9880 *o*-BENZOYLBENZOYL CHLORIDE=A $C_{14}H_9O_2Cl$ A. Beil. X-749
3-CHLORO-3-PHENYLPHTHALIDE=B X_1—
(*o*-Benzoylbenzoyl *pseudo*-chloride) B. Beil. XVII-361
$XVII_1$—



A B

C̄ appears to react in two tautomeric forms corresp to structures A and B, the independent existence of which, however, has not (as yet) been definitely established. The same method of prepn. has in various laboratories given results sometimes suggesting a preponderance of A, sometimes of the tautomer B. The constants reported for C̄ show a correspondingly wide variation, e g., m p. 82–83° (1), abt. 70° (2), 59–60° (3), b p. 170–171° at 1 mm. (1); other workers, e.g. (5) (6), have sometimes obtd. C̄ in crystn form and sometimes not and have failed to report constants

[For prepn. of C̄ from *o*-benzoylbenzoic acid (1·0720) with PCl_5 in CS_2 (2) (3) (4) (5), or PCl_5 (7), PCl_3 (7) (4), or $SOCl_2$ (7) (4) (5) (6) (1) (8) (11), see indic. refs.; for prepn of C̄ from 3-phenylphthalide with Cl_2 at 115–120° see (5)]

C̄-A on htg. above 130° loses HCl and ring-closes yielding (9) (10) anthraquinone (1:9095).

C̄-A with conc. aq NH_4OH at 0° yields (9) *o*-benzoylbenzamide, m p 165° cor. (9), with aniline yields (11) *o*-benzoylbenzanilide, m p 195° (11).

C̄-A with MeOH yields (2) (7) (4) methyl *o*-benzoylbenzoate, m p 51 5° (4), 51 7° (4), 51–52° (2), 52° (12); C̄-B with MeOH yields (7) methyl *pseudo*-*o*-benzoylbenzoate (3-methoxy-3-phenylphthalide), m p 80–81° (7)

C̄-A with EtOH should yield ethyl *o*-benzoylbenzoate, m p. 58° (13) (12); C̄-B with EtOH yields (14) ethyl *pseudo*-*o*-benzoylbenzoate (3-ethoxy-3-phenylphthalide), m p. 51–53° (14), 56° (13).

C̄-A with K phenolate or with phenol in pyridine yields (5) phenyl *o*-benzoylbenzoate, m p. 162–163° (5), C̄-B under same circumstances yields phenyl *pseudo*-*o*-benzoylbenzoate (3-phenoxy-3-phenylphthalide), m.p. 80–82° (5). [For analogous behavior of other phenols see (5).]

C̄-B with phenol yields (6) 3-(*p*-hydroxyphenyl)-3-phenylphthalide, m p. 168–170° (6). [For analogous reactn. with other phenols and phenol ethers see (6)]

[For reactn. of C̄ with α-methylnaphthalene see (15).]

3:9880 (1) Norris, Ware, *J Am. Chem. Soc.* **61**, 1418–1420 (1938) (2) Haller, Guyot, *Bull soc. chim* (3) **25**, 49–56 (1901) (3) Martin, *J. Am Chem. Soc* **38**, 1142–1144 (1916) (4) McMullen, *J. Am. Chem. Soc.* **38**, 1228–1230 (1916) (5) Blicke, Swisher, *J Am. Chem Soc.* **56**, 902–904 (1934). (6) Blicke, Swisher, *J Am Chem Soc* **56**, 923–925 (1934). (7) Meyer, *Monatsh.* **25**, 475–486 (1904). (8) Samdahl, Christiansen, *Bull. soc chim* (5) **5**, 1577 (1938). (9) Graebe, Ullmann, *Ann* **291**, 10–12 (1896). (10) Meyer, *Monatsh.* **25**, 1181–1184 (1904).

(11) Meyer, *Monatsh* **28**, 1226–1227 (1907). (12) Plascuda, *Ber.* **7**, 987 (1874). (13) von Auwers, Heinze, *Ber.* **52**, 599 (1919). (14) Egerer, Meyer, *Monatsh.* **34**, 77–79 (1913). (15) Clar, *Ber.* **63**, 116 (1930)

(11) Ralston, Bauer, *J. Org. Chem.* **5**, 168–169 (1940). (12) Marangoni, *Atti ist. Veneto sci.*, 95–96; *C.A.* **34**, 6934 (1940). (13) Asano, *Cent.* **1931**, II 1867; *C.A.* **25**, 4267 (1931). (15) Brauns, *J. Am. Chem. Soc.* **42**, 1479) Blau, *Monatsh.* **26**, 95–99 (1905). (18) Ralston, Christensen, *Ind. Eng. Chem.* **29**, 194–196 (1937) (19) Ralston, McCorkle, Bauer, *J. Org. Chem.* **5**, 653, 658 (1940). (20) Staudinger, Schwalenstöcker, *Ber.* **68**, 732–741 (1935)
(21) Krafft, Rosiny, *Ber.* **33**, 3577–3578 (1900). (22) Wallace, Copenhaver, *J. Am. Chem. Soc.* **63**, 699 (1941). (23) Holde, Gentner, *Ber.* **58**, 1423 (1925).

3:9890 1-CHLOROPENTADECANE $C_{15}H_{31}Cl$ Beil. I —
(*n*-Pentadecyl chloride) $CH_3.(CH_2)_{13}.CH_2Cl$ I_1-(68)
I_2-(136)

B.P. 168–171° at 10 mm. (1) D^{25}_{25} = **0.8433 (2)** n^{25}_{D} = **1.4470 (2)**

[For prepn. of $\bar{C}$ from *N*-benzoyl-*n*-pentadecylamine (*N*-(*n*-pentadecyl)benzamide) with PCl_5 on distn. (58% yield) see (1); from *n*-$C_{12}H_{25}MgBr$ (1 mole) by reactn. in ether with γ-chloro-*n*-propyl *p*-toluenesulfonate (2 moles) (yield 42% on RMgBr) (note that some 1-bromo-3-chloropropane, b.p. 138–140°, is also formed) see (2).]

[$\bar{C}$ with excess aniline at 100° for a long time, then treated with dil. HCl, ppts. (1) *N*-(*n*-pentadecyl)aniline HCl, cryst. from alc./ether, m.p. 97° (1); free base, m.p 36° (1).]

—— ***n*-Pentadecyl *p*-nitrobenzoate:** m.p. 45.8° cor. (3). [Prepd. indirectly.]
—— ***n*-Pentadecyl 3,5-dinitrobenzoate:** unreported.
—— ***N*-(*n*-Pentadecyl)phthalimide:** unreported.
—— ***S*-(*n*-Pentadecyl isothiourea picrate:** unreported.
—— ***n*-Pentadecyl mercuric chloride:** unreported.

3:9890 (1) von Braun, Solecki, *Ber.* **44**, 1472 (1911). (2) Rossander, Marvel, *J. Am. Chem. Soc.* **50**, 1495 (1928). (3) Armstrong, Copenhaver, *J. Am. Chem. Soc.* **65**, 2252–2253 (1943).

3:9900 PENTADECANOYL CHLORIDE $C_{15}H_{29}OCl$ Beil. S.N. 162

$$CH_3.(CH_2)_{13}.\underset{\displaystyle Cl}{\underset{|}{C}}{=}O$$

B.P. 172–176° at 10 mm. (1)
157° at 5 mm. (2)

[For prepn. of $\bar{C}$ from pentadecanoic acid (1:0620) with $SOCl_2$ (97% yield (1)) see (1).
[For reactn. of $\bar{C}$ with vanillylamine see (2); with 1,7-aminonaphthol see (1).]
$\bar{C}$ on hydrolysis yields pentadecanoic acid (1:0620) q v. (for the amide, anilide, and other derivatives corresp. to $\bar{C}$ see 1:0620).

3:9900 (1) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 86–89, 101 (1939). (2) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 857 (1934).

—— **1-CHLOROHEXADECANE** $CH_3.(CH_2)_{14}.CH_2Cl$ $C_{16}H_{33}Cl$ Beil. I - 172
(*n*-Hexadecyl chloride; I_1—
cetyl chloride) I_2-(138)

B.P. 289° dec. M.P. 15°

See 3:0015. *Division A: Solids.*

(corresp. oxime, m.p. 69.5°; corresp. 2,4-dinitrophenylhydrazone, m.p. 98.0–98.5°; corresp. semicarbazone, m.p. 101° (9)).]

[C̄ with thiophene + $SnCl_4$ gives (yield not stated (18)) 2-furyl *n*-tridecyl ketone (2-myristolythiophene), oil, b.p. 205–210° at 4 mm., $D_{25}^{25} = 0.9506$, $n_D^{25} = 1.4961$ (18).]

[C̄ with carbazole + $AlCl_3$ gives (yield not stated (18)) 2,8-dimyristolylcarbazole, m.p. 169° (18).]

With alcohols. C̄ with alcohols gives in general the corresp. alkyl myristates. [E g , C̄ with MeOH gives methyl myristate (1:2013), m.p. 18.5°; C̄ with EtOH gives ethyl myristate (1:4316), m.p. 11.9°, b p. 295°; etc. — C̄ with benzyl alc. (1:6480) gives (14) benzyl myristate; C̄ with menthol (1:5940) gives (15) menthyl myristate; etc.]

C̄ (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., C̄ with ethylene glycol (1:6465) gives (20) ethylene glycol dimyristate (1:2233), m.p. 63°; C̄ with propanediol-1,2 (1:6455) gives (20) propylene glycol dimyristate, m p. 41.5°; C̄ with butanediol-1,3 (1:6482) gives (20) 1,3-butylene glycol dimyristate, m.p. 29.5–31.0°; C̄ with butanediol-1,4 (1:6516) gives (20) tetramethyleneglycol dimyristate, m.p. 55°].

C̄ has been much employed in prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text [however, for examples of use of C̄ with the compound of glycerol + acetone (i.e., 4-hydroxymethyl-2,2-dimethyldioxolane-1,3) in prepn. of glyceryl α-monomyristate ("α-monomyristin") see (10) (5)].

With phenols. C̄ on htg. with phenols splits out HCl yielding the corresp. esters [e g , C̄ with phenol (1:1420) on htg. gives (7) phenyl myristate, m.p. 36°, b.p. 230° cor. at 15 mm. (7); C̄ with *p*-cresol (1:1410) on htg. gives (7) *p*-tolyl myristate, m.p. 39°, b.p. 239.5° at 15 mm. (7); C̄ (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs. gives (12) pyrocatechol dimyristate, m p. 47–48°; C̄ (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (12) resorcinol dimyristate, m.p. 53°; C̄ (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (12) hydroquinone dimyristate, m.p. 90–90.3°].

[C̄ with phenol (1:1420) + $AlCl_3$ in *sym.*-tetrachloroethane (3:5750) as solvent, however, gives (11) a mixt. of the corresp. hydroxymyristophenones: viz., 31.9% yield (11) *o*-hydroxyphenyl *n*-tridecyl ketone, m.p. 52–55° (corresp. 2,4-dinitrophenylhydrazone, m.p. 92.0–92.5°) and 36.7% yield (11) *p*-hydroxphenyl *n*-tridecyl ketone, m.p. 78–80° (corresp. 2,4-dinitrophenylhydrazone, m.p. 142–143°); for prepn. of these same products by direct rearr. of phenyl myristate (above) with $AlCl_3$ in *sym.*-tetrachloroethane soln. see (19).]

With salts of organic acids. [C̄ with sodium myristate at 100° in absence of air gives (21) myristic anhydride (1:0629), m.p. 53.5° (22), 53 4° (23), 51° (21).]

With organometallic compounds. [C̄ with ethyl sodioacetoacetate gives (60% yield (13)) ethyl α-myristoylacetoacetate, b.p. 170–183° at 3 mm.; this prod. with NH_3 gas splits off the aceto group yielding (13) ethyl myristoylacetate, m.p. 36–37°, b.p. 187–188° at 7 mm.]

With organic amines [illegible]

C̄ with *p*-cymidine

anilide, m p. 88–89

N-(vanillyl)myristamide, α-form, m p. 82°, β-form, m p. 76 5–77°].

C̄ on hydrolysis yields myristic acid (1:0630), m.p. 53 86°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see myristic acid (1:0630).

3:9885 (1) Tecourrou, *Bull. soc. chim.* (5) **6**, 1177, 1180 (1939). (2) Hann, Jamieson, *J. Am. Chem. Soc.* **50**, 1443 (1928). (3) Ralston, Selby, *J. Am Chem. Soc.* **61**, 1019–1020 (1939). (4) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 857 (1934). (5) Rewadikar, Watson, *J. Indian Inst. Sci.* **A-13**, 128–140 (1930). *Cent.* **1930**, II 3737; *C.A.* **25**, 613 (1931). (6) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (7) Krafft, Bürger, *Ber.* **17**, 1378–1380 (1884). (8) Hera-David, Kuster, *Helv. Chim. Acta* **22**, 89 (1939). (9) Ju, Shen, Wood, *J. Inst. Petroleum Tech.* **26**, 514–520 (1940). (10) Averill, Roche, King, *J. Am. Chem. Soc.* **51**, 868 (1929).

[$\bar{C}$ with ethylene + $AlCl_3$ gives a mixt. (87) of mono-, di-, tri-, and tetra-ethyl-*p*-dichlorobenzenes.]

[$\bar{C}$ (3 moles) with $CHCl_3$ (1 mole) + $AlCl_3$ gives (14% yield (88)) *tris*-(2,5-dichlorophenyl)methane, colorless cryst. from C_6H_6, m.p. 206–208° (88). — $\bar{C}$ with CCl_4 + $AlCl_3$ at room temp. (88) or in CS_2 (89) (90) gives (26% yield (88)) 2,5,2',5'-tetrachlorobenzophenone dichloride, m.p 173–174° (89) (88); this with dil. alc. on boilg. or htg. in s.t. at 130° hydrolyzes to 2,5,2',5'-tetrachlorobenzophenone, colorless cryst. from alc., m.p. 128° (89) (90). — $\bar{C}$ with CCl_4 + $AlCl_3$ at 55° for 10 hrs. presumably first yields *tris*-(2,5-dichlorophenyl)methyl chloride (not isolated) which then loses 1 HCl giving (23% yield (88)) 1,4,7-trichloro-9-(2,5-dichlorophenyl)fluorene (?), m.p. 179–180° (88).]

[$\bar{C}$ with acetyl chloride (3:7065) + $AlCl_3$ gives (91) 2,5-dichloroacetophenone, b.p. 251° at 756 mm., m.p. 14° (91) (oxime, m.p. 130°, via Beckmann rearr. with conc. H_2SO_4 gives acet-2,5-dichloroanilide, m.p. 133° (91)). — $\bar{C}$ with benzoyl chloride (3:6240) + $AlCl_3$ yields (91) (92) 2,5-dichlorobenzophenone, white ndls. from alc., m.p. 88° (91), 85–86° (92) (oxime, m.p. on slow htg. 207°, via Beckmann rearr. with conc. H_2SO_4 gives benz-2,5-*dichloroanilide, m.p. 122° (91)). — $\bar{C}$ with o-chlorobenzoyl chloride (3:6640) + $AlCl_3$* gives (92) 2,2',5-trichlorobenzophenone, m.p. 145–147° (92). — $\bar{C}$ with 2,4-dichlorobenzoyl chloride + $AlCl_3$ gives 2,5,2',4'-tetrachlorobenzophenone, m.p. 176° (92).] — [Note that $\bar{C}$ fails to react with *sym*-dichlorodimethyl ether (3:5245).]

[$\bar{C}$ with phthalic anhydride (1:0725) + $AlCl_3$ gives (59.3% (94), 27% (93)) *o*-(2,5-dichlorobenzoyl)benzoic acid, colorless pr. from C_6H_6, m.p. 169° cor. (93), 167° (94); this prod. on ring closure with fumg. H_2SO_4 (94) or conc. H_2SO_4 (93) at 150° gives (yields: 83.5% (94), 83% (93)) 1,4-dichloroanthraquinone [Beil. VII-787, VII_1-(411)], or.-yel. ndls. from AcOH, m.p. 187.5° cor. (93), 186° (94). — Note that $\bar{C}$ reacts with phthalic anhydride + $AlCl_3$ less readily than *o*-dichlorobenzene (3:6055) (use in sepn. of the two isomers (95)). — For corresp. condens. of $\bar{C}$ with 3-sulfophthalic anhydride and 4-sulfophthalic anhydride in pres. of $AlCl_3$ see (96).]

[$\bar{C}$ on partial hydrol. with aq. MeOH alk., alk. carbonates, or best alk. earths in pres. of Cu or Cu salts at elevated temps. under press. gives in excellent yield (98) (99) (100) (101) (102) (103) (104) (105) *p*-chlorophenol (3:0475) (some phenol (1:1420) is also formed (102)); if the hydrolysis of $\bar{C}$ is carried further (100) (106) hydroquinone (1:1590) is also obtd.] — [For study of kinetics of reactn. of $\bar{C}$ with MeOH/alk. see (99) (107) (108).]

[$\bar{C}$ with anhyd. NH_3 in alc. in pres. of $CuCl_2$ + Cu under press. at 150–200° yields (109) *p*-chloroaniline [Beil. XII-607, XII_1-(304)]; $\bar{C}$ with conc. aq. NH_4OH in pres. of CuO under press. at 150–200° gives (110) (111) (112) (113) (114) *p*-phenylenediamine [Beil. XIII-61, $XIII_1$-(18)]. — [$\bar{C}$ with K diphenylamine at 240–245° gives (115) not only the expected *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine, tbls. from acetone, m.p. 199–200°, but also by rearr. *N,N,N',N'*-tetraphenyl-*m*-phenylenediamine, m.p. 137.5–138°.]

[$\bar{C}$ on mononitration, e.g., with 5 wt. pts. abs. HNO_3 at 0° (116) (99), with 2 wt pts. HNO_3 (D = 1.48) below 50° (120), or with 1.5 pts. of a mixt. contg. 2 pts. HNO_3 (D = 1.54) + 3 pts. conc. H_2SO_4 (117) (118) (119) at 70–100° for 30–60 min., yields 1,4-dichloro-2-nitrobenzene [Beil. V-245, V_1-(131)], cryst. from alc , m.p. 55° (120), 54.5° (99), 54° (119), 53° (116) (note close proximity of this m.p. to that of the initial $\bar{C}$).]

[$\bar{C}$ on dinitration, e.g., with 4 wt. pts. fumg. HNO_3 (D = 1.52) + 10 wt. pts. conc. H_2SO_4 at b.p. for 5 hrs. (8) (121), or with 3 wt. pts. HNO_3 (D = 1.52) + 7.5 wt. pts. conc. H_2SO_4 at b.p. for 2 hrs. (122), finally poured into aq., gives a mixt. contg. all three possible dinitro-*p*-dichlorobenzenes; of these the chief prod. is 1,4-dichloro-2,6-dinitrobenzene [Beil. V-265, V_1-(138)], m.p. 106° (123) (119), 105–106° (122), 105° (121), obtd. by recrystn if necessary) of the crude dinitration prod. from 30 p[illegible] . (121); the contain the more soluble 1,4-dichloro-2,3-dinitrob[illegible] [illegible]–103° (122),

3:9912 *n*-HEXADECANOYL CHLORIDE $C_{16}H_{31}OCl$ Beil. II - 374
(Palmitoyl chloride) $CH_3(CH_2)_{14}C(=O)Cl$ II₁-(167) II₂-(341)

B.P.	199–200° at	20 mm.	(1)	M.P. 12° (5) (14)
	194–195° at	17 mm.	(2)	
	198–200° at	16 mm.	(3)	
	192–196° at	15 mm.	(4)	
	192.5° at	15 mm.	(5)	
	191–194° at	14–15 mm.	(6)	
	183–185° at	11 mm.	(7)	
	172° at	5 mm.	(8)	
	139–140° at	1 mm.	(35)	
	162–163° at	0.8 mm.	(9)	
	145–152° at	0.45 mm.	(45)	
	143° at	0.3 mm.	(10)	
	155–160° at	0.2 mm.	(11)	

Note that care must be taken to avoid confusion of C̄ with palmityl chloride (1-chlorohexadecane) (3:0015).

PREPARATION OF C̄

[For prepn. of C̄ from palmitic acid (1:0650) with PCl_5 (yields: 60% (2), 49% (12)) (5) (13) (14) (15) (16), with $PCl_3 + ZnCl_2$ (72% yield (12)), with $SOCl_2$ directly (yields: 93.5% (7), 86% (12), 80% (6)) (17) (19) (45) or in CCl_4 soln. (18), or with phosgene (3:5000) at 140–155° (70–75% yield (20)) see indic. refs.)

CHEMICAL BEHAVIOR OF C̄

Behavior with Inorganic Reactants

With sodium. [C̄ (1 mole) with metallic sodium (1.2 moles) in dry ether refluxed with stirring as directed gives (70% yield (6)) dotriaconten-16-diol-16,17 dipalmitate, i e , the dipalmitate ester of $CH_3(CH_2)_{14}.C(OH){=}C(OH).(CH_2)_{14}CH_3$, cryst. from acetone/$C_6H_6$ (3:1), m.p. 61–62° (6).]

With sodium azide. [C̄ with NaN_3 in C_6H_6 gives (14) palmitoyl azide [Beil. II-375] (not isolated by (14)) which loses N_2 with rearr. to pentadecyl isocyanate [Beil. IV-202] (not isolated by (14) but from indirect prepn. reported (21) as m.p. 8–14°) [cf. corresp. behavior of lauroyl chloride (3:9858)].]

With water. C̄ with aq hydrolyzes to palmitic acid (1:0650) + HCl. [For study of rate of hydrolysis with ord. H_2O and with D_2O see (22).]

Behavior with Organic Reactants

With hydrocarbons. [C̄ with $C_6H_6 + AlCl_3$ gives (60% yield (23)) (24) (25) pentadecyl phenyl ketone (penmitophenone) [Beil. VII-347, VII₁-(186)], lfts. from alc., m.p. 59° (23) (24) (26), b p. 250 5–251.0° at 15 mm. (24) (corresp. oxime, m.p. 73–74° (26)). — C̄ with toluene + $AlCl_3$ gives (24) pentadecyl *p*-tolyl ketone [Beil. VII-347, VII₁-(186)], lfts. from alc., m p. 60° (24) (26), b p. 262° cor. at 15 mm. (24) (corresp. oxime, m p. 60° (27), semicarbazone, m p. 114.5° (26), phenylhydrazone, m p. 54–55° (26)). — For analogous behavior of C̄ + $AlCl_3$ + *m*-xylene (24), mesitylene (27) (2), diphenyl ether (28), and carbazole (28) see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see (28) (29).]

With alcohols. $\bar{C}$ with alcohols gives in general the corresp. alkyl palmitates [e.g., $\bar{C}$ with MeOH gives methyl palmitate (1:2055), m.p. 30°; $\bar{C}$ with EtOH gives ethyl palmitate (1:2034), α-form, m.p. 19.4°, β-form, m.p. 24.2°, etc.; $\bar{C}$ with bezynl alc. (1:6480) gives (30) benzyl palmitate, m.p. 36°; $\bar{C}$ with menthol (1:5940) gives (31) menthyl palmitate, m.p. 32°].

$\bar{C}$ (2 moles) with dihydric alcs. on htg. gives the corresp. neutral esters [e.g., $\bar{C}$ with ethylene glycol (1:6465) gives (32) ethylene glycol dipalmitate (1:2269), m.p. 70.5°; $\bar{C}$ with propanediol-1,2 (1:6455) gives (32) propylene glycol dipalmitate, m.p. 52.5–54.5°; $\bar{C}$ with butanediol-1,3 (1:6482) gives (32) 1,3-butylene glycol dipalmitate, m.p. 39–40°; $\bar{C}$ with butanediol-1,4 (1:6516) gives (32) tetramethylene glycol dipalmitate, m.p. 63°].

$\bar{C}$ has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. $\bar{C}$ on htg. with phenols splits out HCl yielding the corresp. esters. [E.g., $\bar{C}$ with phenol (1:1420) gives (5) phenyl palmitate, m.p. 45° (5), 44.5–46.0° (33), b.p. 249.5° at 15 mm. (5); $\bar{C}$ with *p*-cresol (1:1410) gives (5) *p*-tolyl palmitate, m.p. 47°, b.p. 258° at 15 mm. — $\bar{C}$ (2 moles) with pyrocatechol (1:1520) at 110° for 2 hrs gives (34) pyrocatechol dipalmitate, m.p. 58°; $\bar{C}$ (2 moles) with resorcinol (1:1530) at 110° for 2 hrs. gives (34) resorcinol dipalmitate, m.p. 62.5–63.5°; $\bar{C}$ (2 moles) with hydroquinone (1:1590) at 110° for 2 hrs. gives (34) hydroquinone dipalmitate, m.p. 94.5°.]

[$\bar{C}$ with phenol (1:1420) + $AlCl_3$ in *sym.*-tetrachloroethane (3:5750) as solvent, however, gives (35) (33) (36) a mixt. of the corresp. hydroxypalmitophenones; viz., 25.4% yield *o*-hydroxyphenyl pentadecyl ketone, m.p. 54–56° (corresp. 2,4-dinitrophenylhydrazone, m.p. 94–95° (35)), and 28.5% yield *p*-hydroxyphenyl pentadecyl ketone, m.p. 84.5–85° (35), 78° (37) (corresp. 2,4-dinitrophenylhydrazone, m.p. 141–142° (35)); for study of influence upon *o/p* ratio of use of nitrobenzene and of CS_2 as solvents see (36).]

With salts of organic acids. [$\bar{C}$ with Ag palmitate at 100° for 10 min. (38) or $\bar{C}$ with Na$\bar{A}$ (32) (42) gives palmitic anhydride (1:0651), m.p. 64° (39), 63.9° (40), 63–64° (41), 63° (38), 62–63° (32) (43), but the latter is usually prepd. from palmitic acid (1:0650) by htg. with Ac_2O (39) (40) (41) (42) (43).]

With esters. [$\bar{C}$ with diethyl sodiomalonate would be expected to give diethyl palmitoylmalonate, but for unsuccessful attempt to realize this reaction see (44).]

[$\bar{C}$ with ethyl sodio-acetoacetate in dry ether gives (62% yield (11)) (45) ethyl α-palmitoylacetoacetate, m.p. 36–36.5° (11) (45); note that this prod. with aq. NaOH splits off the acetyl group giving (62% yield (11)) ethyl palmitoylacetate, m.p. 37–38° (11) (45).]

With amines. $\bar{C}$ with org. prim. amines yields the corresp. amides [e.g., $\bar{C}$ with *p*-cymidine (2-methyl-5-isopropylaniline) gives (1) palmito-(2-methyl-5-isopropyl)anilide, m.p. 90–91°; $\bar{C}$ with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (8) *N*-(vanillyl)-palmitamide, α-form, m.p. 89–89.5°, β-form, m.p. 84–84.5°].

$\bar{C}$ on hydrolysis yields palmitic acid (1:0650), m.p. 62.7°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to $\bar{C}$ see palmitic acid (1:0650).

3:9912 (1) Hann, Jamieson, *J. Am. Chem. Soc.* **50**, 1443 (1928). (2) Klages, *Ber.* **35**, 2260–2261 (1902). (3) Stephenson, *Biochem. J.* **7**, 431 (1913). (4) Gault, Ehrmann, *Bull. soc. chim.* (4) **39**, 876 (1926). (5) Krafft, Bürger, *Ber.* **17**, 1379–1380 (1884). (6) Ralston, Selby, *J. Am. Chem. Soc.* **61**, 1019–1020 (1939). (7) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 89 (1939). (8) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 857 (1934). (9) Fischer, Bergmann, Bärwind, *Ber.* **53**, 1603 (1920). (10) Nishimura, *Science Repts. Tohoku Imp. Univ.* **20**, 97–100 (1931); *Cent.* **1931**, I 3671; *C.A.* **25**, 3978 (1931).

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Ger. 281,364, Jan. 2, 1915; *Cent.* **1915**, I 230; *C.A.* **9**, 2130 (1915). (19) Izard, *Biochem. Z.* **40**, 402 (1912). (20) Prat, Étienne, *Bull. soc. chim.* (5) **11**, 30–34 (1944); *C.A.* **38**, 6274 (1944).
(21) Jeffreys, *Am. Chem. J.* **22**, 27 (1899). (22) Hughes, Rideal, *J. Chem. Soc.* **1934**, 1107. (23) Adam, *Proc. Roy. Soc.* (*London*) **A-103**, 684–685 (1923). (24) Krafft, *Ber* **19**, 2982–2983 (1886). (25) I.G., French 693,699, Nov. 24, 1930; *Cent.* **1931**, I 1018; [*C.A.* **25**, 1646 (1931)]. (26) Ryan, Nolan, *Proc. Roy. Irish Acad.* **30-B**, 1–7 (1912); *Cent.* **1913**, II 2050; *C.A.* **7**, 1712 (1913). (27) Claus, Häfelin, *J. prakt. Chem.* (2) **54**, 402–403 (1896). (28) Ralston, Christensen, *Ind. Eng. Chem.* **29**, 194–196 (1937). (29) Ralston, Christensen (to Armour and Co), U.S. 2,033,541, March 10, 1936; *Cent.* **1936**, II 897; [*C.A.* **30**, 3131 (1936)]. (30) Shonle, Row, *J. Am. Chem Soc.* **43**, 363 (1921).
(31) F [illegible]
733–742
Atti ist. [illegible]
(1910).
J. Org. C [illegible]
Soc. **193** [illegible]
J. Am. Chem. Soc. **63**, 699 (1941).
(41) Holde, Gentner, *Ber.* **58**, 1424 (1925). (42) Krafft, Rosiny, *Ber.* **33**, 3578 (1900). (43) Autenrieth, Thomae, *Ber.* **57**, 430 (1924) (44) von Auwers, Jacobsen, *Ann.* **426**, 222 (1922). (45) Helferich, Köster, *Ber.* **56**, 2090–2091 (1923).

—— 1-CHLOROHEPTADECANE $CH_3(CH_2)_{15}.CH_2Cl$ $C_{17}H_{35}Cl$ **Beil. I —**
(*n*-Heptadecyl chloride) I_1-(60)
I_2—

B.P. 192–195° at 10 mm. M.P. 24°

See 3:0100. *Division A: Solids.*

3:9925 n-HEPTADECANOYL CHLORIDE $C_{17}H_{33}OCl$ **Beil. S.N. 162**
(*n*-Margaroyl chloride) $CH_3.(CH_2)_{15}-\underset{\displaystyle Cl}{\underset{|}{C}}=O$

B.P. 176° at 4 mm. (1)
139–144° at 0.04 mm. (2)

[For prepn. of C̄ from margaric acid (1:0635) with $SOCl_2$ (84.5% yield (2)) (1) (3) see indic. refs.]

C̄ with phenol (1:1420) on htg. gives (3) phenyl margarate, cryst. from MeOH, m.p. 37°, b.p. 240–250° dec. at 11 mm. (3).

[C̄ with alkali margarates presumably would yield margaric anhydride, cryst. from ether or pet. ether, m.p. 67.6° cor. (4), although this reaction has not actually been reported and the margaric anhydride is readily obtd. from the acid (1:0635) with Ac_2O (4).]

[For reaction of C̄ with vanillylamine see (1); with 1,7-aminonaphthol see (2).]

C̄ on hydrolysis yields margaric acid (1:0635); for the amide and other derivs. corresp. to C̄ see margaric acid (1:0635).

3:9925 (1) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 858 (1934). (2) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 89, 101 (1939) (3) Skraup, Schwamberger, *Ann.* **462**, 153 (1928). (4) Wallace, Copenhaver, *J. Am. Chem. Soc.* **63**, 699–700 (1941).

—— 1-CHLORO-OCTADECANE $CH_3(CH_2)_{16}CH_2Cl$ $C_{18}H_{37}Cl$ **Beil. S.N. 10**
(*n*-Octadecyl chloride;
stearyl chloride)

B.P. 180–190° at 12 mm. M.P. 21°

See 3:0095 *Division A: Solids*

3:9940 *n*-**OLEOYL CHLORIDE** $C_{18}H_{33}OCl$ Beil. II - 469
(*cis*-Octadecen-9-oyl chloride) II_1-(204)
II_2—

$CH_3(CH_2)_7$—CH
‖
$Cl.C.(CH_2)_7$—CH
‖
O

B.P. 213°	at 13.5 mm.	(1)
200°	at 11 mm.	(2)
163°	at 2 mm.	(3)
170–175°	at 0.42 mm.	(4)
158–159°	at 0.05 mm.	(5)

[*See also the trans stereoisomer, viz., elaidoyl chloride* (3:9950).]

[For prepn. of C̄ from oleic acid (1:0565) with PCl_5 (yields: 75% (2), 48% (6), 27% (7)) (8), with PCl_3 (46% yield (6)) (9), with $PCl_3 + ZnCl_2$ (50% yield (7)), with $SOCl_2$ (yields: 82.5% (4), 80% (7), 75% (2)) (3), with oxalyl (di)chloride (3:5060) (90% yield (3)), or with $COCl_2$ (3:5000) (10) see indic. refs.]

Note that C̄ with oleic acid (1:0565) forms a const.-boilg. mixt., b.p. about 241° at 6 mm., contg. 40% C̄ (6).

The *reaction of C̄ as an acyl chloride with a wide variety of organic compounds* has been reported in many patents which cannot be reviewed here.

C̄ has also been employed in the course of prepn. of mixed glycerides; although this topic cannot be fully reviewed in this text, see for examples (3) (11) (12).

[For behavior of C̄ with resins derived from indene, coumarone, or dicyclopentadiene see (13).]

[C̄ with diazomethane gives an intermediate diazoketone which on decompn. with AcOH gives (75% yield (4)) nonadecen-10-one-2-yl-1 acetate, m.p. 21° (14).]

[C̄ with phenol (1:1420) at 160° for 4 hrs. gives (55% yield (18)) phenyl oleate, oil, b.p. 256–257° at 12 mm. (18).]

[C̄ with Na oleate yields (10) oleic anhydride [Beil. II-469, II_2-(441)], lfts. or scales from ether or alc., m.p. 22.2° (15), 22° (16), but the latter is usually prepared directly (15) (17) from oleic acid (1:0565).]

C̄ on hydrolysis yields oleic acid (1:0565); for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see oleic acid (1:0565).

[illegible] *Chem.* 27, 40 (1914). [illegible] *Roy. Soc. Can.* (3) 27, III 97–103 (1933). (8) Shonle, Row, *J. Am. Chem. Soc.* 43, 363 (1921). (9) Aschan, *Ber.* 31, 2349 (1898). (10) Prat, Étienne, *Bull. soc. chim.* (5) 11, 30–34 (1944); *C.A.* 38, 6274 (1944). [illegible] 65, 2144–2145 (1943). (12) Jackson, [illegible] –290 (1944). (13) Ralston, Vander Wal, [illegible]). (14) Grundmann, *Ann.* 524, 31–39 [illegible] Levene, Rolf, *J. Biol. Chem.* 60, 681 (1924). (17) Holde, Smelkus, *Ber.* 53, 1894–1895 (1920). (18) Skraup, Beng, *Ber.* 60, 950 (1927).

3:9950 ELAIDYL CHLORIDE $C_{18}H_{33}OCl$ Beil. II - 470
II_1—
II_2—

$CH_3.(CH_2)_7$—C—H Cl
‖ |
H—C—$(CH_2)_7$.C=O

B.P. 216°	at 13 mm.	(1) sl. dec.
168–170°	at 1 mm.	(5)

[For prepn. of C̄ from elaidic acid (1:0610) with PCl_5 (1), with $SOCl_2$ (2), or with oxalyl (di)chloride (3:5060) (91% yield (5)) cf. (6) see indic. refs.]

[For reactn. of C̄ with diazomethane giving (83% yield (2)) 1-diazononadecen-10-one-2, m.p. 53° (2), see (2); for reactn. of C̄ with ethyl sodio-acetosuccinate see (3); for use of C̄ in prepn. of synthetic glycerides see (4).]

C̄ on hydrolysis yields elaidic acid (1:0610) (for the amide and other derivatives corresp. to C̄ see 1:0610).

3:9950 (1) Krafft, Tritschler, *Ber.* **33**, 3582 (1900). (2) Grundmann, *Ann.* **524**, 43 (1936). (3) Robinson, *J. Chem Soc.* **1930**, 750. (4) Böhmer, Kappeller, *Fette u. Seifen* **44**, 340–343 (1937); *Cent.* **1938**, I 573. (5) Daubert, *J. Am Chem Soc.* **66**, 291 (1944). (6) Wood, Jackson, Baldwin, Longenecker, *J. Am. Chem. Soc.* **66**, 287–289 (1944).

3:9960 *n*-OCTADECANOYL CHLORIDE (Stearoyl chloride)

$C_{18}H_{35}OCl$ — $CH_3(CH_2)_{16}—C(=O)—Cl$

Beil. II - 384; II_1-(176); II_2-(360)

B.P.				M.P.	
215°	at	15 mm.	(1)	24°	(2)
211–219°	at	15 mm.	(2)	23°	(1)
200–215°	at	13–15 mm.	(3)	23.2–23.4°	(8)
205°	at	9 mm.	(4)		
202–203°	at	6 mm.	(5)		
180–190°	at	5–6 mm.	(45)		
203°	at	5 mm.	(6)		
185°	at	3 mm.	(7)		
195–195.5°	at	2 mm.	(8)		
161–166°	at	0.5–1.0 mm.	(9)		
176–178°	at	0.5 mm.	(10)		
165°	at	0.4 mm.	(11)		

Note that care must be taken to avoid confusion of C̄ with stearyl chloride (1-chloro-octadecane) (3:0095).

PREPARATION OF C̄

[For prepn. of C̄ from stearic acid (1:0660) with PCl_5 directly (1) (12) (13) (21) or in CCl_4 soln. (14), with $SOCl_2$ directly (yields: 97% (10), 81% (3)) (4) (7) (15) (16) (17) or in CCl_4 soln. (yield 86% (8)) (14), with PCl_3 (18), with oxalyl (di)chloride (3:5060) (11), or with phosgene (3:5000) at 140–150° (70–75% yield (19)) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Behavior with Inorganic Reagents

Hydrogenation of C̄. [C̄ with H_2 + $Pd/BaSO_4$ cat. in boilg. xylene gives (20) (21) stearaldehyde (1:0012).]

Behavior with bromine. [For behavior of C̄ with Br_2 at room temp., 100°, and 135° see (22).]

Behavior with sodium. [C̄ (1 mole) with metallic sodium (1.2 moles) in dry ether under reflux gives (67% yield (3)) hexatriaconten-18-diol-18,19 distearate, i.e., the distearate ester of $CH_3(CH_2)_{16}C(OH)=C(OH)(CH_2)_{16}CH_3$, m.p. 67–68°.]

With sodium azide. [C̄ with NaN_3 in C_6H_6 gives (23) (12) stearoyl azide (not isolated) which loses N_2 with rearr. giving (43% yield (23)) heptadecyl isocyanate, b.p. 208–209°

at 17 mm. (23), 200–203° at 15 mm. (24); cf. the corresp. behavior of lauroyl chloride (3:9858).]

With water. C̄ with aq. hydrolyzes to stearic acid (1:0660) + HCl.

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons (or their equivalents). [C̄ with C_6H_6 + $AlCl_3$ gives (yields: 65% (25), 60% (26)) (27) (18) heptadecyl phenyl ketone (stearophenone) [Beil. VII-347, VII_1-(187)], lfts. from alc., m.p. 64–65° (25), 63 5–64.5° (18), 64° (28), 59° (27) (29) (corresp. oxime, m.p. 53° (27), phenylhydrazone, m.p. 54° (28)); note that in this reaction no introduction of a second acyl radical occurs (30), and that attempts to prepare stearophenone by use (with C_6H_6 + $AlCl_3$) of the mixed anhydride from stearic acid with ketene) gave very poor yields (29). — For patents on the use of stearophenone as an electric insulator (31), on its sulfonation (32), or on its reaction with PCl_3 (33) see indic. refs.]

[C̄ with toluene + $AlCl_3$ gives (34) heptadecyl *p*-tolyl-ketone [Beil. VII-347, VII_1-(187)], lfts. from alc., m.p. 67° (34), 66–67° (28), b.p. 278° cor. at 15 mm. (34) (corresp. oxime, m.p. 64° (27)). — For analogous behavior of C̄ with naphthalene (1:7200) (18), tetralin (1:7550) (18), biphenyl (1:7175) (18) (35), *p*-methylbiphenyl (35), *p*-chlorobiphenyl (3:1912) (35), diphenyl ether (1:7125) (35), *p*-nitrodiphenyl ether (35), furan (1:8015) (35), 2-methylfuran (35), dibenzofuran (35), thiophene (35), dibenzothiophene (35), carbazole (35), etc., see indic. refs.; for use of these products as waxes, addition agents for lubricants, etc., see (35) (36).]

[For behavior of C̄ with resins derived from indene, coumarone, or dicyclopentadiene see (37). — For addition of C̄ to alkynes in pres. of a condensing agent such as $AlCl_3$, $ZnCl_2$, etc., see (38) cf. (39).]

With alcohols. C̄ with alcohols gives in general the corresp. alkyl stearates. [E g, C̄ with MeOH gives methyl stearate (1:2095), m.p. 38.8°; C̄ with EtOH gives ethyl stearate (1:2078), α-form, m.p. 30.9°, β-form, m.p. 33.5°. — C̄ with benzyl alc. (1:6480) gives (40) benzyl stearate, m.p. 45 8°; C̄ with menthol (1:5940) gives (41) menthyl stearate, m.p. 38–39°.]

C̄ has also been much employed in the prepn. of mixed glycerides, but this topic cannot be expanded in detail in this text.

With phenols. [C̄ on htg. with phenols splits out HCl yielding the corresp. esters: e.g, C̄ with phenol (1:1420) gives (1) phenyl stearate, m.p. 52° (1), 51.5–53.0 (44), b.p. 267° at 15 mm. (1); C̄ with *p*-cresol (1:1410) gives (1) *p*-tolyl stearate, m.p. 54°, b p. 276° at 15 mm.]

[C̄ (2 moles) with pyrocatechol (1:1520) at 100° gives (42) (43) pyrocatechol distearate, m.p. 83–85° (43), 68° (42); C̄ (2 moles) with hydroquinone (1:1590) at 130° gives (42) hydroquinone distearate, m.p. 97°.]

[C̄ with phenol (1:1420) + $AlCl_3$ in *sym*-tetrachloroethane (3:5750) as solvent, however, gives (45) (44) (46) a mixt. of the corresp. hydroxystearophenones: viz., 27.8% yield *o*-hydroxyphenyl heptadecyl ketone, m.p. 64–66° (corresp. 2,4-dinitrophenylhydrazone, m.p. 96–97° (45)); and 28% yield *p*-hydroxyphenyl heptadecyl ketone, m.p. 87–89° corresp. 2,4-dinitrophenylhydrazone, m.p. 139.5–140° (45)); for study of influence upon *o/p* ratio of use of nitrobenzene or of CS_2 as solvents see (46).]

With salts of organic acids. [C̄ with Ag stearate at 100° for 10 min. gives (47) stearic anhydride (1:4915), m.p. 71–72° (48), 71–71.5° (49), 70.7° (50), 70.5° (47), 70–71° (51), but the latter is usually prepd. from stearic acid (1:0660) by htg. with Ac_2O (48) (49) (50) (51).]

With esters. [C̄ with ethyl sodio-acetoacetate refluxed 1 hr. under N_2 gives (68% yield (52)) ethyl α-stearoylacetoacetate, m.p. 42°; note that this prod. with aq. NaOH splits off its acetyl group giving (74% yield (52)) ethyl stearoylacetate, m.p. 46 5° (corresp. copper enolate, m.p. 111–112°).]

With Grignard reagents. [C̄ with *ter*-BuMgBr gives (28.5% yield (8)) *ter*-butyl *n*-heptadecyl ketone, m.p. 44.8–45.1° (corresp. semicarbazone, m.p. 78.0–78 2°); note that low yield suggests probability that the RMgBr also acted as a reducing agent cf. corresp. behavior of lauroyl chloride (3:9858), but no study of such effect for this combination is reported. — C̄ with cyclohexyl MgBr gives (8) cyclohexyl *n*-heptadecyl ketone.]

[C̄ with EtMgBr + $CdCl_2$ (53) or C̄ with $ZnEt_2$ (54) gives (65% yield (53)) ethyl *n*-heptadecyl ketone (eikosanone-3) [Beil. I-719, I_1-(374), I_2-(774)], m p 60–61° (54), 59.5–60° (55), 57° (28), 54–55° (53) (corresp. oxime, m p. 55.5–56.5° (54), semicarbazone, m.p. 89–91° (53))]

With diazomethane. [C̄ with CH_2N_2 (2 2 moles) as directed gives (88.5% yield (15)) 1-diazononadecanone-2, m.p. 69°, which in AcOH loses N_2 and esterifies giving (89% yield (15)) nonadecanon-2-yl-l acetate, m.p. 72°.]

With amines. C̄ with org. prim. amines yields the corresp. amides [e g., C̄ with *p*-cymidine (2-methyl-5-isopropylaniline) gives (56) stearo-(2-methyl-5-isopropyl)anilide, m.p. 93–94°; C̄ with vanillylamine (4-hydroxy-3-methoxybenzylamine) gives (5) *N*-(vanillyl)-stearamide, α-form, m.p 94 5–95°, β-form, m.p. 90.0–90 5°].

C̄ on hydrolysis yields stearic acid (1:0660), m.p. 69–70°; for the amide, anilide, *p*-toluidide, and other derivatives corresp. to C̄ see stearic acid (1:0660).

3:9960 (1) Krafft, Bürger, *Ber.* **17**, 1379–1380 (1884). (2) Gault, Ehrmann, *Bull. soc. chim.* (4) **39**, 876 (1926). (3) Ralston, Selby, *J. Am. Chem Soc.* **61**, 1019–1020 (1939). (4) Ott, Zimmermann, *Ann.* **425**, 337 (1921). (5) Ford-Moore, Phillips, *Rec. trav. chim.* **53**, 858 (1934). (6) Kabashima, *Ber.* **71**, 1072 (1938). (7) Robinson, Roche, King, *J. Am. Chem Soc.* **54**, 707 (1932). (8) Strating, Backer, *Rec. trav. chim* **55**, 909, 914 (1936). (9) Fischer, Bergmann, Bärwind, *Ber.* **53**, 1597 (1920). (10) Fierz-David, Kuster, *Helv. Chim Acta* **22**, 89 (1939).

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(51) Autenrieth, Thomae, *Ber.* **57**, 429 (1924). (52) Bergel, Jacob, Todd, Work, *J. Chem. Soc.* **1938**, 1378. (53) Gilman, Nelson, *Rec. trav. chim.* **55**, 528–530 (1936). (54) Ponzio, de Gaspari, *Gazz. chim. ital.* **29**, I 474 (1899). (55) Saville, Shearer, *J. Chem. Soc.* **127**, 593 (1925). (56) Hann, Jamieson, *J. Am. Chem. Soc.* **50**, 1443 (1928).

CHAPTER XXIII

I. INDEX OF COMPOUNDS ACCORDING TO EMPIRICAL FORMULA

This Empirical Formula Index comprises four parts as follows:

A. Compounds containing only carbon and chlorine.
B. Compounds containing only carbon, oxygen, and chlorine.
C. Compounds containing only carbon, hydrogen, and chlorine.
D. Compounds containing only carbon, hydrogen, oxygen, and chlorine.

Within each section the component individuals are arranged in groups according to increasing number of carbon atoms. Within each group of isomeric compounds the order of listing follows the sequence of the eight units comprising the Chemical Type Index.

A. COMPOUNDS CONTAINING ONLY CARBON AND CHLORINE

C_1 GROUP

CCl_4 M.W. = 153.8 Cl = 92.2%
Carbon tetrachloride **3:5100**

C_2 GROUP

C_2Cl_2 M.W. = 94.9 Cl = 74.7%
Dichloroacetylene **3:5010**

C_2Cl_4 M.W. = 165.8 Cl = 85.5%
Tetrachloroethylene **3:5460**

C_2Cl_6 M.W. = 236.8 Cl = 89.9%
Hexachloroethane **3:4835**

C_3 GROUP

C_3Cl_6 M.W. = 248.8 Cl = 85.5%
Hexachloropropene **3:6370**

C_3Cl_8 M.W. = 319.7 Cl = 88.7%
Octachloropropane **3:4450**

C_4 GROUP

C_4Cl_2 M.W. = 119.0 Cl = 59.6%
1,4-Dichlorobutadi-yne-1,3 **3:9040**

C_4Cl_6 M.W. = 260.8 Cl = 81.6%
Hexachlorobutadiene-1,3 **3:6425**

C_5 GROUP

C_5Cl_8 M.W. = 343.7 Cl = 82.5%
Octachlorocyclopentene **3:0422**

C_6 GROUP

C_6Cl_6 M.W. = 284.8 Cl = 74.7%
Hexachlorobenzene **3:4939**

C_{10} GROUP

$C_{10}Cl_8$ M.W. = 403.8 Cl = 70.3%
Octachloronaphthalene **3:4893**

B. COMPOUNDS CONTAINING ONLY CARBON, OXYGEN, AND CHLORINE

C_1 GROUP

$COCl_2$ M.W. = 98.9 Cl = 71.7%
Carbonyl chloride (phosgene) **3:5000**

C_2 GROUP

C_2OCl_4 M.W. = 181.8 Cl = 78.0%
Trichloroacetyl chloride **3:5420**

$C_2O_2Cl_2$ M.W. = 126.9 Cl = 55.9%
Oxalyl (di)chloride **3:5060**

$C_2O_2Cl_4$ M.W. = 197.8 Cl = 71.7%
Trichloromethyl chloroformate (diphosgene) **3:5515**

C_3 GROUP

C_3OCl_4 M.W.=193 9 Cl=73.2%
Trichloroacryloyl chloride **3:5845**

C_3OCl_6 M.W.=124.1 Cl=58.1%
Hexachloroacetone **3:6312**
Pentachloropropionyl chloride **3:0470**

$C_3O_2Cl_6$ M.W.=280.8 Cl=75.8%
Trichloromethyl trichloroacetate **3:0290**

$C_3O_3Cl_6$ M.W.=296.8 Cl=71.7%
Di-(trichloromethyl) carbonate (triphosgene) **3:1915**

C_4 GROUP

C_4OCl_6 M.W.=276.8 Cl=76 9%
Di-(trichlorovinyl) ether **3:6373**

C_4OCl_{10} M.W.=418 6 Cl=84.7%
Decachlorodiethyl ether **3:1676**

$C_4O_2Cl_4$ M.W.=221.9 Cl=63.9%
Dichloromaleyl (di)chloride **3:6197**

$C_4O_3Cl_2$ M.W.=167.0 Cl=42.5%
Dichloromaleic anhydride **3:3635**

$C_4O_3Cl_6$ M.W.=308.8 Cl=68.9%
Trichloroacetic acid anhydride **3:6575**

C_6 GROUP

C_6OCl_6 M.W.=300.8 Cl=70.0%
"Hexachlorophenol" **3:3180**

$C_6O_2Cl_4$ M.W.=245.9 Cl=57.7%
Tetrachlorobenzoquinone-1,2 **3:3965**
Tetrachlorobenzoquinone-1,4 (chloranil) **3:4978**

$C_6O_2Cl_6$ M.W.=316.8 Cl=67.2%
2,3,5,5,6,6-Hexachloro-cyclohexen-2-dione-1,4 **3:3260**
"Hexachloro*resorcinol*" ***3:3470***

C_7 GROUP

C_7OCl_6 M.W.=312.8 Cl=68 0%
Pentachlorobenzoyl chloride **3:2295**

C_8 GROUP

$C_8O_3Cl_4$ M W.=285.9 Cl=49 6%
Tetrachlorophthalic anhydride **3:4947**

C. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, AND CHLORIDE

C_1 GROUP

$CHCl_3$ M.W.=119.4 Cl=89.1%
Chloroform **3:5050**

CH_2Cl_2 *M.W.=84.9 Cl=83 5%*
Methylene (di)chloride **3:5020**

CH_3Cl M.W.=50 5 Cl=70 2%
Methyl chloride **3:7005**

C_2 GROUP

C_2HCl M.W.=60.5 Cl=58.6%
Chloroacetylene **3:7000**

C_2HCl_3 M.W.=131.4 Cl=81.0%
Trichloroethylene **3:5170**

C_2HCl_5 M.W.=202.3 Cl=87.6%
Pentachloroethane **3:5880**

$C_2H_2Cl_2$ M.W.=97.0 Cl=73.1%
1,1-Dichloroethylene (vinylidene (di)chloride) **3:5005**
1,2-Dichloroethylene (*cis* form) **3:5042**
1,2-Dichloroethylene (*trans* form) **3:5028**
1,2-Dichloroethylene (ord. mixt.) **3:5030**

$C_2H_2Cl_4$ M.W.=167.9 Cl=84 5%
1,1,1,2-Tetrachloroethane **3:5555**
1,1,2,2-Tetrachloroethane **3:5750**

C_2H_3Cl M.W.= 62.5 Cl=56.7%
Vinyl chloride **3:7010**

$C_2H_3Cl_3$ M.W.=133.4 Cl=79.7%
1,1,1-Tri*chloroethane* **3:5085**
1,1,2-Trichloroethane **3:5330**

$C_2H_4Cl_2$ M.W.=99.0 Cl=71.7%
1,1-Dichloroethane **3:5035**
1,2-Dichloroethane **3:5130**

C_2H_5Cl M.W.=64.5 Cl=55.1%
Ethyl chloride ***3:7015***

C_3 GROUP

C_3HCl_5 M.W.=214 3 Cl=82 7%
1,1,2,3,3-Petachloropropene-1 **3:6075**

C_3HCl_7 M.W.=285.2 Cl=87.0%
1,1,1,2,2,3,3-Heptachloropropane **3:0200**
1,1,1,2,3,3,3-Heptachloropropane ***3:6860***

$C_3H_2Cl_4$ M.W.=179.9 Cl=78 8%
1,2,3,3-Tetrachloropropene-1 **3:5920**

$C_3H_2Cl_6$ M.W.=250 8 Cl=84 8%
1,1,1,2,3,3-Hexachloropropane **3:6460**
1,1,2,2,3,3-Hexachloropropane ***3:6525***

C_3H_3Cl M.W.=74.5 Cl=47.6%
3-Chloropropyne-1 ***3:7100***

101° (121), and 1,4-dichloro-2,5-dinitrobenzene, m.p. 119° (122) (121) (124). — For f.p. compn. data and diagrams of mixtures of the 2,6- and 2,3-dinitro-*p*-dichlorobenzenes see (119), of mixtures of the 2,6- and 2,5-dinitro-*p*-dichlorobenzenes see (121). — Note also that the prod., m.p. 81°, formerly (8) supposed to be the 2,5-dinitro isomer, has since (121) been proved to be a compound of the 2,6- and 2,5-dinitro-1,4-dichlorobenzenes. — The relative proportion of the three dinitration products varies with conditions (119) (121) (122) (124).]

[C̄ on monosulfonation, e.g., with 1.5 wt. pts. fumg. H_2SO_4 (10–12% SO_3) at 140–150° for 45 min. (118) cf. (27), gives on pouring into aq (85–90% yield (118)) 1,4-dichlorobenzenesulfonic acid-2, cryst. from aq. as monohydrate (for derivs see below). — Note that C̄ is not sulfonated by conc. H_2SO_4 even at 210° (16) (dif. from *o*-dichlorobenzene (3:6055) and use in sepn. from C̄); for removal of chlorobenzene (3:7903) from mixt. with dichlorobenzenes via sulfonation of former with 95% H_2SO_4 see (17) — For use of reactn. prod. of C̄ with SO_2 as dye intermed. or for mothproofing of wool see (125). — For reactn. of sodium *p*-dichlorobenzenesulfonate with fused NaOH to yield hydroquinone (1:1590) see (126).]

[*C̄ with 5 moles $ClSO_3H$ at 150° for 1 hr. (127) (128) gives (85% yield (127) (128)) 1,4-dichlorobenzenesulfonyl chloride-2, cryst. from lgr., m.p. 39° (127) (128), 38° (129), 36.8° (27) (corresp. amide, see below; corresp. sulfonanilide, m.p. 160° (128)); for use in* prepn. of tetrachlorothioindigo see (130) — C̄ with 30 pts $ClSO_3H$ at 140° for 48 hrs. (128) gives both 1,4-dichlorobenzene-*bis*-(sulfonyl chloride)-2,6, m.p. 114° (corresp. *bis*-sulfonanilide, m.p. 215–217° dec (128)) and 1,4-dichlorobenzene-*bis*-(sulfonyl chloride)-2,5, m.p. 182° (corresp. *bis*-sulfonanilide, m.p. not given). — Note that C̄ reacts with $ClSO_3H$ much less easily than *o*-dichlorobenzene; for use in sepn. of the two isomers via formn. of *o*-dichlorobenzenesulfonyl chloride and sepn. from unchanged C̄ by distn. see (131).]

Ⓓ **1,4-Dichlorobenzenesulfonamide-2** (2,5-dichlorobenzenesulfonamide-1): cryst. from dil. alc., m.p. 179.5–180° u.c. (129), 181° (127), 185–186° (27) [From C̄ via treatment with $ClSO_3H$ as directed (129) to 1,4-dichlorobenzenesulfonyl chloride-2 (see above) and subsequent conv with $(NH_4)_2CO_3$ to desired sulfonamide.] — [Note that, although the m.p. of this sulfonamide is practically identical with that from *m*-dichlorobenzene (3:5960), each depresses the m.p. of a mixt with the other; the m.p.'s of the precursor sulfonyl chlorides, viz 52–53° for the isomer from *m*-dichlorobenzene, 38° for that from C̄, may also serve to distinguish them (129).] — [For similar prepn. and use of 1,4-dichlorobenzenesulfonamide-2 see (132).]

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C_4 GROUP

C_9 GROUP

C_8 GROUP

$C_8H_{15}Cl$ M.W. = 146.7 Cl =
2-Chloro-octene-1
3-Chloro-octene-1

2-Chloro-octene-2
4-Chloro-octene-2

4-Chloro-octene-4

4-Chloro-6-methylheptene-1

6-Chloro-2-methylheptene-2

4-Chloro-3-methylheptene-2

4-Chloro-6-methylheptene-2

5-Chloro-4-methylheptene-3

4-Chloro-2,5-dimethylhexene-2

4-Chloro-3,5-dimethylhexene-2

2-Chloro-2,5-dimethylhexene-3

1-Chloro-4-ethylhexene-3

2-Chloro-3-ethyl-3-methylpentene-1

$C_8H_{16}Cl_2$ M.W. = 183.1 Cl =
1,6-Dichloro-octane
1,7-Dichloro-octane
1,8-Dichloro-octane
2,2-Dichloro-octane

4-Chloro-3-(chloromethyl)heptane

2,5-Dichloro-2,5-dimethylhexane

3,4-Dichloro-3,4-dimethylhexane

3,3-Dichloro-2,2,4-trimethylpentane

$C_8H_{17}Cl$ M.W. = 148.7 Cl =
1-Chloro-octane
2-Chloro-octane
4-Chloro-octane

2-Chloro-2-methylheptane
6-Chloro-2-methylheptane

3-Chloro-3-methylheptane
3-(*Chloromethyl*)heptane

3-Chloro-4-methylheptane
4-Chloro-4-methylheptane

1-Chloro-3-ethylhexane
3-Chloro-3-ethylhexane

3-Chloro-2,3-dimethylhexane
2-Chloro-2,5-dimethylhexane

$C_{12}H_{25}Cl$ M.W. = 204.8 Cl = 17.3%
1-Chlorododecane **3:8810**

C_{13} GROUP

$C_{13}H_{10}Cl_2$ M.W. = 237.1 Cl = 29.9%
Benzophenone dichloride **3:6960**
4,4′-Dichlorodiphenylmethane **3:1057**

$C_{13}H_{11}Cl$ M.W. = 202.7 Cl = 17.5%
Benzohydryl chloride **3:0060**

$C_{13}H_{27}Cl$ M.W. = 218.8 Cl = 16 2%
1-Chlorotridecane **3:9859**

C_{14} GROUP

$C_{14}H_8Cl_2$ M.W. = 247.1 Cl = 28.7%
9,10-Dichloroanthracene **3:4916**

$C_{14}H_8Cl_4$ M.W. = 318.0 Cl = 44 6%
1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene **3:19250**

1,1-Dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene **3:9863**

1,1-Dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene **3:2438**

$C_{14}H_8Cl_6$ M.W. = 388.9 Cl = 54.7%
1,1,1,2-Tetrachloro-2,2-*bis*-(*p*-chlorophenyl)ethane **3:2477**

$C_{14}H_9Cl_3$ M.W. = 283.6 Cl = 37.5%
1-Chloro-2,2-*bis*-(*p*-chlorophenyl)-ethylene **3:1430**

$C_{14}H_9Cl_5$ M.W. = 354 5 Cl = 50 0%
"*o,o′*-DDT" **3:9865**
"*o,p′*-DDT" **3:1820**
"*m,p′*-DDT" **3:9867**
"*p,p′*-DDT" (ordinary DDT) **3:3298**

$C_{14}H_{10}Cl_2$ M.W. = 249 1 Cl = 28 5%
1,1-Dichloro-2,2-diphenylethylene **3:1938**
1,1-Di-(*p*-chlorophenyl)ethylene **3:2475**

cis-1,2-Dichloro-1,2-diphenylethylene **3:1380**
trans-1,2-Dichloro-1,2-diphenylethylene **3:4210**

$C_{14}H_{10}Cl_4$ M.W. = 320.1 Cl = 44.3%
1,1,2,2-Tetrachloro-1,2-diphenylethane **3:4496**
1,1-Dichloro-2-(*o*-chlorophenyl)-ethane **3:1890**
1,1-Dichloro-2,2-*bis*-(*p*-chlorophenyl)ethane **3:3320**

$C_{14}H_{11}Cl_3$ M.W. = 285 6 Cl = 37.2%
1,1,1-Trichloro-2,2-diphenylethane **3:1420**

$C_{14}H_{12}Cl_2$ M.W. = 251.2 Cl = 28.3%
1,1-Di-(*p*-chlorophenyl)ethane **3:0995**

1,1-Dichloro-2,2-diphenylethane **3:1940**

d,l-1,2-Dichloro-1,2-diphenylethane **3:2570**
meso-1,2-Dichloro-1,2-diphenylethane **3:4854**

$C_{14}H_{13}Cl$ M.W. = 216 7 Cl = 11.7%
1,1-Diphenylethyl chloride **3:9870**
2,2-Diphenylethyl chloride **3:9871**

$C_{14}H_{29}Cl$ M.W. = 232.8 Cl = 15.2%
1-Chlorotetradecane **3:9874**

C_{15} GROUP

$C_{15}H_{31}Cl$ M.W. = 246 9 Cl = 14 4%
1-Chloropentadecane **3:9890**

C_{16} GROUP

$C_{16}H_{33}Cl$ M.W. = 260.9 Cl = 13.6%
1-Chlorohexadecane **3:0015**

C_{17} GROUP

$C_{17}H_{35}Cl$ M.W. = 274.9 Cl = 12 9%
1-Chloroheptadecane **3:0100**

C_{18} GROUP

$C_{18}H_{37}Cl$ M.W. = 288.9 Cl = 12.3%
1-Chloro-octadecane **3:0095**

C_{19} GROUP

$C_{19}H_{15}Cl$ M.W. = 278.8 Cl = 12 7%
Triphenylchloromethane **3:3410**

C_{20} GROUP

$C_{20}H_{15}Cl$ M.W. = 290 8 Cl = 12.2%
1-Chloro-1,2,2-triphenylethylene **3:3560**

D. COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, OXYGEN, AND CHLORINE

C_2 GROUP

C_2HOCl_3 M.W. = 147.4 Cl = 72.2%
Trichloroacetaldehyde (chloral) **3:5210**

Dichloroacetyl chloride **3:5290**

$C_2HO_2Cl_3$ M.W. = 163.4 Cl = 65.1%
Trichloroacetic acid **3:1150**

Dichloromethyl chloroformate **3:5315**

$C_2H_2OCl_2$ M.W. = 112.9 Cl = 62.8%
Dichloroacetaldehyde **3:5180**

Chloroacetyl chloride **3:5235**

$C_2H_2O_2Cl_2$ M.W. = 128.9 Cl = 55 0%
Dichloroacetic acid **3:6208**

(31) Jaeger, *Z. anorg. allgem. Chem.* **101**, 115 (1917). (32) Quick, *J. Am. Chem. Soc.* **42**, 1035–1040 (1920). (33) von Auwers, *Ann.* **422**, 164 (1921). (34) Hendricks, *Z. Krist.* **84**, 85–96 (1932). (35) Huggins, *J. Am. Chem. Soc.* **45**, 272 (1923). (36) von Auwers, *Z. physik. Chem.* **30**, 312 (1899). (37) Menschutkin, *J. Russ. Phys.-Chem. Soc.* **43**, 416 (1911); *Cent.* **1911**, II 379–381. (38) Deffet, *Bull. soc. chim. Belg.* **47**, 464–470 (1938). (39) Vuks, *Acta Physicochim. U.R.S.S.* **6**, 327–338 (1937). (40) Meyer, *Rec. trav. chim.* **42**, 306–312 (1923).

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C_5 GROUP

C_7 GROUP

C_9 GROUP

C_{10} GROUP

[illegible] 1925 II 1800. (112) Williams [illegible] 95. (113) Federal Phos- [illegible] oth (to Swann Research, [illegible] ssermann, Bauer, *Ber.* 32, [illegible] –40 (1901). (116) Booy, [illegible] m. *Soc.* 81, 1382 (1902). [illegible]

U.S. 2,171,166, Aug. 29, 19[illegible] 1929; *C.A.* 36, 2158 (1942). (120) von Bramer [illegible] 4, 1922; *Cent.* 1924, I 2823; *C.A.* 16, 2867 (19[illegible] –2558 (1922). (128) Gebauer-Fülnegg, Figdor, *Monatsh.* 48, 627–637 (1927); Gebauer-Fülnegg, Neumann, *Monatsh.* 50, 236 (1928). (129) Huntress, Carten, *J. Am. Chem. Soc.* 62, 511–514 (1940). (130) United Alkali Co., Dodd, Sprent, Brit. 251,321, May 27, 1926; *Cent.* 1926, II 2356.

(131) Imperial Chem. Ind., & Bennet, Brit. 440,205, Jan. 23, 1936, *Cent.* 1936, I 4367. (132) Kyrides (to Monsanto Chem. Co.), U.S. 1,993,722, March 5, 1935; *Cent.* 1935, II 1446.

3:0985 18-CHLORO-OCTADECANOL-1 $C_{18}H_{37}OCl$ Beil. S.N. 24

(ω-Chloro-*n*-octadecyl alcohol; ω-chlorostearyl alcohol)

$CH_2.(CH_2)_{16}.CH_2OH$ with Cl on the first CH_2

M.P. 53–54.5° (1)

Colorless crystals.

[For prepn. from α,ω-octadecamethylene glycol (m.p. 97–98°) with $SOCl_2$ + dimethylaniline in C_6H_6 (50% yield) see (1); note that a little 1,18-dichloro-octadecane with m.p. 54° (i.e., practically the same as Č) is also formed.]

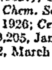
Č is only slightly attacked by KOH (2).

Ⓓ 18-Chloro-octadecyl *N*-phenylcarbamate: lfts. from alc. or lt. pet., m.p. 77° (1).

3:0985 (1) Bennett, Gudgeon, *J. Chem. Soc.* 1938, 1679–1681. (2) Seck, Dittmar, *Chem. Umschau Fette, Öle, Wachse, Harze* 39, 226–229 (1932); *Cent.* 1933, I 1757, [*C.A.* 27, 703 (1933)].

3:0990 1,2,3-TRICHLOROBENZENE $C_6H_3Cl_3$ Beil. V - 203

(*vic*-Trichlorobenzene) V₁-(112) V₂-(150)



M.P. 54°	(1)	**B.P. 218–219° (3)**
53–54°	(2) (3)	
52.3–53.0°	(4)	
52.4°	(5)	
52°	(6)	
50.8°	(7)	

Tbls. from alc.; eas. sol. CS_2 or C_6H_6; spar. sol. alc.; volatile with steam. [For use as component of mixtures for dif. inflammable electric insulating materials see (8).] [For thermal anal. of mixts. of Č with 1,2,4-trichlorobenzene (3:6420) and with 1,3,5-trichlorobenzene (3:1400) see (5).]

[For prepn. of Č from 2,3,4-trichloroaniline [Beil. XII-626] with ethyl nitrite (3) or by diazotization and reaction with alc. (35% yield (4)), or from 3,4,5-trichloroaniline [Beil.

II. INDEX OF EMPIRICAL FORMULAS ACCORDING TO PERCENTAGE CHLORINE CONTENT

The empirical formulas for all groups of isomers listed in this book are represented below in diminishing order of their percentage chlorine. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their molecular weights comprises Index III (page 1383).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume, see the Empirical Formula Index (page 1359).

% Chlorine	Formula	% Chlorine	Formula	% Chlorine	Formula
92.2	CCl_4	76.9	C_4OCl_6	68.0	C_7OCl_6
89 9	C_2Cl_6	75.8	$C_3O_2Cl_6$	67.6	$C_4H_3Cl_3$
89.1	$CHCl_3$	74.7	C_2Cl_2	67.6	$C_5H_8Cl_4$
88.7	C_3Cl_8	74.7	C_6Cl_6	67.2	$C_6O_2Cl_6$
87.6	C_2HCl_5	74.5	C_7HCl_7	67.1	$C_7H_3Cl_5$
87.0	C_3HCl_7	73.9	$C_4H_2Cl_4$	66 9	$C_3H_2O_2Cl_4$
85 5	C_2Cl_4	73.2	C_3OCl_4	66.7	$C_4H_5Cl_3$
85.5	C_3Cl_6	73.1	$C_2H_2Cl_2$	66.6	C_6HOCl_5
85.0	$C_4H_2Cl_8$	73.1	$C_3H_3Cl_3$	65.9	$C_3H_3OCl_3$
84.8	$C_3H_2Cl_6$	73.1	$C_4H_4Cl_4$	65.9	$C_4H_7Cl_3$
84.7	C_4OCl_{10}	73.1	$C_6H_6Cl_6$	65.9	$C_5H_2O_3Cl_6$
84.5	$C_2H_2Cl_4$	72.5	$C_5H_7Cl_5$	65.7	$C_6H_2Cl_4$
83.5	CH_2Cl_2	72.4	$C_3H_2OCl_4$	65.1	$C_2HO_2Cl_3$
82.9	$C_4H_3Cl_7$	72 4	$C_4H_6Cl_4$	64.5	$C_3H_5OCl_3$
82.7	C_3HCl_5	72.2	C_2HOCl_3	64.5	$C_6H_6Cl_4$
82.5	C_5Cl_8	72.1	$C_3H_5Cl_3$	64 3	$C_2H_3O_2Cl_3$
82.0	$C_3H_3Cl_5$	72.0	$C_3HO_2Cl_5$	63.9	$C_3H_4Cl_2$
81.6	C_4Cl_6	71.7	$COCl_2$	63.9	$C_4O_2Cl_4$
81.1	$C_4H_2OCl_8$	71.7	$C_2O_2Cl_4$	63.7	C_7HOCl_5
81.0	C_2HCl_3	71.7	$C_2H_4Cl_2$	63.3	$C_4H_2O_2Cl_4$
81.0	$C_4H_2Cl_6$	71.7	$C_3O_3Cl_6$	63.3	$C_6H_{10}Cl_4$
80.3	$C_4H_4Cl_6$	71.7	$C_3H_4OCl_4$	62 8	$C_2H_2OCl_2$
79.7	$C_2H_3Cl_3$	71.2	$C_2H_3OCl_3$	62.8	$C_3H_6Cl_2$
78.8	$C_3H_2Cl_4$	71.2	$C_7H_2Cl_6$	62 8	$C_4H_4O_2Cl_4$
78.3	C_4HCl_5	70.8	C_6HCl_5	61.7	$C_3H_4OCl_2$
78.0	C_2OCl_4	70.7	C_6OCl_6	61.7	$C_7H_4Cl_4$
78.0	$C_3H_4Cl_4$	70.3	$C_{10}Cl_8$	61.3	$C_5H_7Cl_3$
77.6	$C_4H_3Cl_5$	70.2	CH_3Cl	61.2	$C_6H_2OCl_4$
77.0	C_3HOCl_5	68.9	$C_4O_3Cl_6$	60 6	$C_3HO_2Cl_3$
77.0	$C_4H_5Cl_5$	68 6	$C_6H_9Cl_5$	60.6	$C_4H_5OCl_3$

% Chlorine	Formula
28.7	$C_{14}H_8Cl_2$
28.5	$C_4H_9O_2Cl$
28.5	$C_{14}H_{10}Cl_2$
28.3	$C_{14}H_{12}Cl_2$
28.2	$C_{13}H_8OCl_2$
28.0	C_7H_7Cl
27.6	C_6H_5OCl
27.6	C_7H_9Cl
27.2	$C_5H_3O_2Cl$
27.1	$C_7H_{11}Cl$
26.8	C_4HO_3Cl
26.8	$C_{14}H_{10}OCl_2$
26.7	C_6H_9OCl
26.7	$C_7H_{13}Cl$
26.4	$C_5H_7O_2Cl$
26 3	$C_6H_{11}OCl$
26.3	$C_7H_{15}Cl$
26.0	$C_4H_5O_3Cl$
26.0	$C_5H_9O_2Cl$
26.0	$C_6H_{13}OCl$
25.6	$C_4H_7O_3Cl$
25.6	C_8H_7Cl
25.2	C_7H_5OCl
25.2	C_8H_9Cl
25 2	$C_{14}H_{10}O_2Cl_2$
25.1	C_8H_5Cl
24 9	$C_6H_3O_2Cl$
24.9	C_7H_7OCl
24.5	$C_6H_5O_2Cl$
24.5	$C_8H_{13}Cl$
24.2	$C_7H_{11}OCl$
24.2	$C_8H_{15}Cl$
23.9	$C_6H_9O_2Cl$
23.9	$C_7H_{13}OCl$
23.9	$C_8H_{17}Cl$
23.6	$C_4H_3O_4Cl$
23.5	$C_5H_7O_3Cl$
23.5	$C_6H_{11}O_2Cl$
23.5	$C_7H_{15}OCl$
23.2	$C_5H_9O_3Cl$
23.2	$C_6H_{13}O_2Cl$
23.2	C_9H_9Cl
22.9	C_8H_7OCl
22 9	$C_9H_{11}Cl$
22.7	$C_7H_5O_2Cl$
22.6	C_8H_9OCl
22.4	$C_9H_{15}Cl$
22.1	$C_9H_{17}Cl$
21.8	$C_7H_{11}O_2Cl$
21.8	$C_8H_{15}OCl$
21.8	$C_9H_{19}Cl$
21.8	$C_{10}H_7Cl$
21.5	$C_6H_9O_3Cl$
21.5	$C_7H_{13}O_2Cl$
21.5	$C_8H_{17}OCl$
21.5	C_9H_5OCl
21.3	$C_7H_{15}O_2Cl$
21.3	C_9H_7OCl
21.0	C_9H_9OCl
21.0	$C_{10}H_{13}Cl$
20.8	$C_8H_7O_2Cl$
20.8	$C_9H_{11}OCl$
20.6	$C_7H_5O_3Cl$
20.5	$C_{10}H_{17}Cl$
20.3	$C_{10}H_{19}Cl$
20.1	$C_9H_{17}OCl$
20.1	$C_{10}H_{21}Cl$
20.1	$C_{11}H_9Cl$
19 9	$C_6H_7O_4Cl$
19.9	$C_8H_{15}O_2Cl$
19.8	$C_9H_{19}OCl$
19.8	$C_{10}H_7OCl$
19 6	$C_8H_{17}O_2Cl$
19 6	$C_9H_5O_2Cl$
19.4	$C_6H_{11}O_4Cl$
19.4	$C_8H_3O_3Cl$
19.4	$C_{10}H_{11}OCl$
19.2	$C_8H_5O_3Cl$
19.2	$C_9H_9O_2Cl$
19.2	$C_{10}H_{13}OCl$
19.0	$C_8H_7O_3Cl$
18.8	$C_{12}H_9Cl$
18.6	$C_{10}H_{19}OCl$
18.6	$C_{11}H_{23}Cl$
18.6	$C_{11}H_7OCl$
18.5	$C_{10}H_4O_2Cl_2$
18.4	$C_{10}H_5O_2Cl$
18.4	$C_{10}H_{21}OCl$
18.2	$C_7H_{11}O_4Cl$
17.7	$C_8H_5O_4Cl$
17.7	$C_{10}H_{13}O_2Cl$
17.5	$C_{13}H_{11}Cl$
17.3	$C_{11}H_{21}OCl$
17.3	$C_{12}H_9OCl$
17.3	$C_{12}H_{25}Cl$
17.2	$C_8H_{11}O_4Cl$
17.2	$C_{11}H_7O_2Cl$
16.4	$C_{13}H_9OCl$
16.2	$C_{12}H_{23}OCl$
16.2	$C_{13}H_{27}Cl$
16.1	$C_{12}H_{25}OCl$
15.6	$C_8H_{15}O_5Cl$
15.4	$C_{14}H_{11}OCl$
15.2	$C_{13}H_{25}OCl$
15.2	$C_{14}H_{29}Cl$
15.1	$C_{11}H_{19}O_3Cl$
14.6	$C_{14}H_7O_2Cl$
14.5	$C_{14}H_9O_2Cl$
14.4	$C_9H_5O_6Cl$
14.4	$C_{14}H_{11}O_2Cl$
14.4	$C_{14}H_{27}OCl$
14.4	$C_{15}H_{31}Cl$
14.2	$C_{14}H_{29}OCl$
13.6	$C_{15}H_{29}OCl$
13.6	$C_{16}H_{33}Cl$
12.9	$C_{16}H_{31}OCl$
12.9	$C_{17}H_{35}Cl$
12 8	$C_{16}H_{33}OCl$
12.7	$C_{19}H_{15}Cl$
12.3	$C_{17}H_{33}OCl$
12.3	$C_{18}H_{37}Cl$
12.2	$C_{10}H_{15}Cl$
11.8	$C_{18}H_{33}OCl$
11.7	$C_{18}H_{35}OCl$
11.7	$C_{14}H_{13}Cl$
11.6	$C_{18}H_{37}OCl$

% Chlorine	Formula	% Chlorine	Formula	% Chlorine	Formula
60.6	$C_5H_9Cl_3$	48.0	$C_5H_7O_3Cl_3$	38.3	C_4H_9Cl
60.2	$C_7HO_2Cl_5$	48.0	$C_6H_{11}O_2Cl_3$	37.9	$C_4H_4O_4Cl_2$
59.9	$C_4H_7OCl_3$	47.6	C_3H_3Cl	37.9	$C_5H_8O_3Cl_2$
59.6	C_4Cl_2	47.6	$C_6H_6Cl_2$	37.9	$C_6H_{12}O_2Cl_2$
59.2	$C_4H_2O_3Cl_4$	47.6	$C_8H_5OCl_3$	37.5	$C_2H_3O_2Cl$
58.6	C_2HCl	47.2	$C_7H_3O_2Cl_3$	37.5	C_3H_7OCl
58.6	$C_6H_3Cl_3$	47.2	$C_8H_7OCl_3$	37.5	$C_8H_6OCl_2$
58.1	C_3OCl_6	47.0	$C_6H_8Cl_2$	37.5	$C_{14}H_9Cl_3$
58.1	$C_7H_2OCl_4$	46.7	$C_8H_2O_4Cl_4$	37.2	$C_{14}H_{11}Cl_3$
58.0	$C_6H_5Cl_3$	46.4	$C_4H_2O_2Cl_2$	37.1	$C_7H_4O_2Cl_2$
57.7	$C_4H_4Cl_2$	46.4	$C_6H_3O_3Cl_3$	37.1	$C_8H_8OCl_2$
57.7	$C_6O_2Cl_4$	46.3	C_3H_5Cl	36.0	$C_7H_{10}O_2Cl_2$
57.4	$C_6H_7Cl_3$	46.3	$C_6H_{10}Cl_2$	36.0	$C_9H_{18}Cl_2$
57.2	$C_6H_2O_2Cl_4$	46.0	$C_{10}H_5Cl_3$	36.0	$C_{10}H_6Cl_2$
56.8	$C_4HO_2Cl_3$	45.7	$C_4H_4O_2Cl_2$	34.9	$C_8H_4O_2Cl_2$
56.7	C_2H_3Cl	45.7	$C_5H_8OCl_2$	34.6	C_6H_7Cl
56.7	$C_4H_6Cl_2$	45.7	$C_6H_{12}Cl_2$	34.3	$C_7H_4O_3Cl_2$
56.7	$C_6H_9Cl_3$	45.6	$C_7H_{11}O_2Cl_3$	33.9	C_3HO_2Cl
56.0	$C_3H_3O_2Cl_3$	45.2	C_2H_3OCl	33.9	C_4H_5OCl
55.9	$C_2O_2Cl_2$	45.2	$C_4H_6O_2Cl_2$	33.9	C_5H_9Cl
55.9	$C_3H_4OCl_2$	45.2	$C_6H_9O_3Cl_3$	33.9	$C_6H_2O_4Cl_2$
55.8	$C_4H_8Cl_2$	45.1	C_3H_7Cl	33.6	$C_8H_{12}O_2Cl_2$
55.6	$C_4H_5O_2Cl_3$	44.6	$C_4H_8O_2Cl_2$	33.6	$C_{10}H_{20}Cl_2$
55.1	C_2H_5Cl	44.6	$C_{14}H_8Cl_4$	33.3	$C_3H_3O_2Cl$
55.0	$C_2H_2O_2Cl_2$	44.3	$C_{14}H_{10}Cl_4$	33.3	C_4H_7OCl
55.0	$C_3H_6OCl_2$	44.0	C_2H_5OCl	33.3	$C_5H_{11}Cl$
55.0	$C_4H_7O_2Cl_3$	44.0	$C_7H_6Cl_2$	33.3	$C_{10}H_6OCl_2$
54.7	$C_{14}H_8Cl_6$	43.5	$C_6H_4OCl_2$	33.3	$C_{12}H_{21}O_2Cl_3$
54.6	$C_7H_2O_2Cl_4$	42.5	$C_4O_3Cl_2$	33.0	$C_6H_8O_4Cl_2$
54.4	$C_7H_5Cl_3$	42.0	$C_5H_6O_2Cl_2$	33.0	$C_7H_{12}O_3Cl_2$
54.2	$C_2H_4O_2Cl_2$	41.9	$C_7H_{14}Cl_2$	32.7	$C_3H_5O_2Cl$
53.9	$C_6H_3OCl_3$	41.6	$C_6H_{12}OCl_2$	32.7	C_4H_9OCl
52.5	$C_{10}H_8Cl_4$	41.6	$C_8H_5O_3Cl_3$	32.7	$C_8H_2O_3Cl_2$
51.8	$C_5H_6Cl_2$	41.5	$C_4H_4O_3Cl_2$	32.1	$C_3H_7O_2Cl$
51.8	$C_5H_7O_2Cl_3$	41.5	$C_5H_8O_2Cl_2$	32.1	$C_8H_6O_3Cl_2$
51.3	$C_4H_5O_3Cl_3$	41.0	C_4H_3Cl	31.8	$C_{12}H_8Cl_2$
51.0	$C_5H_8Cl_2$	41.0	$C_4H_6O_3Cl_2$	31.5	C_6H_5Cl
50.8	$C_7H_3OCl_3$	40.5	$C_7H_4OCl_2$	31.5	$C_9H_{14}O_2Cl_2$
50.3	$C_3H_2O_2Cl_2$	40.5	$C_8H_8Cl_2$	30.4	C_6H_9Cl
50.3	$C_4H_6OCl_2$	40.1	C_4H_5Cl	30.2	$C_8H_4O_4Cl_2$
50.3	$C_5H_{10}Cl_2$	40.1	$C_6H_2O_2Cl_2$	29.9	C_5H_7OCl
50.3	$C_6HO_2Cl_3$	40.1	$C_7H_6OCl_2$	29.9	$C_6H_{11}Cl$
50.3	$C_7H_5OCl_3$	39.6	$C_6H_4O_2Cl_2$	29.9	$C_{12}H_{10}Cl_2$
50.0	$C_{14}H_9Cl_5$	39.6	$C_8H_{12}Cl_2$	29.7	$C_{10}H_{16}O_2Cl_2$
49.8	$C_6H_3O_2Cl_3$	39.2	C_3H_3OCl	29.6	$C_8H_{12}O_4Cl_2$
49.6	$C_3H_4O_2Cl_2$	39.2	C_4H_7Cl	29.4	$C_4H_5O_2Cl$
49.6	$C_4H_8OCl_2$	38.7	$C_6H_8O_2Cl_2$	29.4	C_5H_9OCl
49.6	$C_8O_3Cl_4$	38.7	$C_8H_{16}Cl_2$	29.4	$C_6H_{13}Cl$
48.6	$C_6H_9O_2Cl_3$	38.3	C_3H_5OCl	28.9	$C_4H_7O_2Cl$
48.2	$C_6H_4Cl_2$	38.3	$C_4H_2O_4Cl_2$	28.9	$C_5H_{11}OCl$

M.W.	Formula	M.W.	Formula	M.W.	Formula
152.6	$C_5H_9O_3Cl$	173.0	$C_4H_6O_3Cl_2$	191.1	$C_8H_8OCl_2$
152.6	$C_6H_{13}O_2Cl$	173.5	$C_5H_7Cl_3$	191.5	$C_4H_5O_2Cl_3$
152 6	C_9H_9Cl	174.7	$C_{10}H_{19}Cl$	191.6	$C_{10}H_4O_2Cl_2$
153.0	$C_4H_2O_2Cl_2$	175 0	$C_7H_4OCl_2$	191.9	$C_4H_2Cl_4$
153.1	$C_6H_{10}Cl_2$	175.1	$C_8H_8Cl_2$	192.6	$C_{10}H_5O_2Cl$
153.8	CCl_4	175.4	$C_3HO_2Cl_3$	192.6	$C_{10}H_{21}OCl$
154.6	C_8H_7OCl	175.5	$C_4H_5OCl_3$	193.5	$C_4H_7O_2Cl_3$
154.6	$C_9H_{11}Cl$	175.5	$C_5H_9Cl_3$	193.9	C_3OCl_4
155 0	$C_4H_4O_2Cl_2$	176.6	$C_{11}H_9Cl$	193.9	$C_4H_4Cl_4$
155.0	$C_5H_8OCl_2$	176.7	$C_9H_{17}OCl$	194.6	$C_7H_{11}O_4Cl$
155.1	$C_6H_{12}Cl_2$	176.7	$C_{10}H_{21}Cl$	195.5	$C_7H_5Cl_3$
156 6	$C_7H_5O_2Cl$	177.0	$C_6H_2O_2Cl_2$	195.9	$C_3H_2OCl_4$
156.6	C_8H_9OCl	177.0	$C_7H_6OCl_2$	195.9	$C_4H_6Cl_4$
157.0	$C_4H_6O_2Cl_2$	177.4	$C_3H_3O_2Cl_3$	197.1	$C_7H_{10}O_2Cl_2$
157.4	$C_4H_3Cl_3$	177.5	$C_4H_7OCl_3$	197.1	$C_9H_{18}Cl_2$
158.7	$C_9H_{15}Cl$	178.6	$C_6H_7O_4Cl$	197.1	$C_{10}H_6Cl_2$
159.0	$C_4H_8O_2Cl_2$	178.6	$C_{10}H_7OCl$	197.5	$C_6H_3OCl_3$
159.5	$C_4H_5Cl_3$	178.7	$C_8H_{15}O_2Cl$	197.8	$C_2O_2Cl_4$
160.7	$C_9H_{17}Cl$	178.7	$C_9H_{19}OCl$	197.9	$C_3H_4OCl_4$
161.0	$C_7H_6Cl_2$	179.0	$C_6H_4O_2Cl_2$	200.6	$C_8H_5O_4Cl$
161.4	$C_3H_3OCl_3$	179.1	$C_8H_{12}Cl_2$	200.7	$C_{10}H_{13}O_2Cl$
161.5	$C_4H_7Cl_3$	179 9	$C_3H_2Cl_4$	202.3	C_2HCl_5
162.6	$C_7H_{11}O_2Cl$	180.6	$C_9H_5O_2Cl$	202.7	$C_{13}H_{11}Cl$
162.6	$C_{10}H_7Cl$	180.7	$C_8H_{17}O_2Cl$	203.0	$C_8H_4O_2Cl_2$
162.7	$C_8H_{15}OCl$	181.5	$C_6H_3Cl_3$	204.7	$C_{11}H_{21}OCl$
162.7	$C_9H_{19}Cl$	181.8	C_2OCl_4	204.7	$C_{12}H_9OCl$
163.0	$C_6H_4OCl_2$	181.9	$C_3H_4Cl_4$	204 8	$C_{12}H_{25}Cl$
163.4	$C_2HO_2Cl_3$	182.6	$C_6H_{11}O_4Cl$	205 5	$C_5H_7O_2Cl_3$
163.4	$C_3H_5OCl_3$	182.6	$C_8H_3O_3Cl$	206.6	$C_8H_{11}O_4Cl$
164.6	$C_6H_9O_3Cl$	182.6	$C_{10}H_{11}OCl$	206.6	$C_{11}H_7O_2Cl$
164.6	$C_7H_{13}O_2Cl$	183.0	$C_6H_8O_2Cl_2$	207.0	$C_7H_4O_3Cl_2$
164 6	C_9H_5OCl	183.1	$C_8H_{16}Cl_2$	207.5	$C_4H_5O_3Cl_3$
164 7	$C_8H_{17}OCl$	183.5	$C_6H_5Cl_3$	209.0	$C_6H_2O_4Cl_2$
165 4	$C_2H_3O_2Cl_3$	184.6	$C_8H_5O_3Cl$	209.5	$C_7H_3OCl_3$
165.8	C_2Cl_4	184.6	$C_9H_9O_2Cl$	209.9	$C_5H_8Cl_4$
166.6	C_9H_7OCl	184.7	$C_{10}H_{13}OCl$	211.1	$C_8H_{12}O_2Cl_2$
166 7	$C_7H_{15}O_2Cl$	185.0	$C_4H_2O_4Cl_2$	211.2	$C_{10}H_{20}Cl_2$
167.0	$C_4O_3Cl_2$	185.5	$C_6H_7Cl_3$	211.4	$C_6HO_2Cl_3$
167.9	$C_2H_2Cl_4$	186.6	$C_8H_7O_3Cl$	211.5	$C_7H_5OCl_3$
168.6	C_9H_9OCl	187.0	$C_4H_4O_4Cl_2$	211.9	$C_3H_2O_2Cl_4$
168.7	$C_{10}H_{13}Cl$	187.0	$C_5H_8O_3Cl_2$	213.1	$C_{10}H_6OCl_2$
169.0	$C_5H_6O_2Cl_2$	187.1	$C_6H_{12}O_2Cl_2$	213.5	$C_6H_3O_2Cl_3$
169.1	$C_7H_{14}Cl_2$	187.4	$C_4HO_2Cl_3$	214.3	C_3HCl_5
170.6	$C_8H_7O_2Cl$	187.5	$C_6H_9Cl_3$	215.0	$C_6H_8O_4Cl_2$
170.6	$C_9H_{11}OCl$	188.7	$C_{12}H_9Cl$	215.1	$C_7H_{12}O_3Cl_2$
171.0	$C_4H_4O_3Cl_2$	189 0	$C_8H_6OCl_2$	215.9	$C_6H_2Cl_4$
171.0	$C_5H_8O_2Cl_2$	190.6	$C_{11}H_7OCl$	216.3	$C_3H_3Cl_5$
171.1	$C_6H_{12}OCl_2$	190.7	$C_{10}H_{19}OCl$	216.7	$C_{13}H_9OCl$
172.6	$C_7H_5O_3Cl$	190.8	$C_{11}H_{23}Cl$	216.7	$C_{14}H_{13}Cl$
172.7	$C_{10}H_{17}Cl$	191.0	$C_7H_4O_2Cl_2$	217.0	$C_8H_2O_3Cl_2$

III. INDEX OF EMPIRICAL FORMULAS ACCORDING TO MOLECULAR WEIGHTS

The empirical formulas for all groups of isomers listed in this book are represented below in increasing order of their molecular weights. Note that there are numerous instances in which this value is the same for several different formulas. An analogous list of empirical formulas arranged according to their percentage chlorine comprises Index II (page 1380).

To ascertain which specific compounds corresponding to a given formula are described in the text of this volume see the Empirical Formula Index (page 1359).

M.W.	Formula	M.W.	Formula	M.W.	Formula
50.5	CH_3Cl	113.0	$C_3H_6Cl_2$	134.5	$C_4H_3O_3Cl$
60.5	C_2HCl	115.0	$C_2H_4OCl_2$	136.6	$C_5H_9O_2Cl$
62.5	C_2H_3Cl	116.6	C_6H_9Cl	136.6	$C_6H_{13}OCl$
64.5	C_2H_5Cl	118.6	C_5H_7OCl	136.6	C_8H_5Cl
74.5	C_3H_3Cl	118.6	$C_6H_{11}Cl$	137.0	$C_5H_6Cl_2$
76.5	C_3H_5Cl	119.0	C_4Cl_2	138.6	$C_4H_7O_3Cl$
78.5	C_2H_3OCl	119.4	$CHCl_3$	138.6	C_8H_7Cl
78.5	C_3H_7Cl	120.5	$C_4H_5O_2Cl$	139.0	$C_5H_8Cl_2$
80.5	C_2H_5OCl	120.6	C_5H_9OCl	140.6	C_7H_5OCl
84.9	CH_2Cl_2	120.6	$C_6H_{13}Cl$	140.6	C_8H_9Cl
86.5	C_4H_3Cl	122.6	$C_4H_7O_2Cl$	141.0	$C_3H_2O_2Cl_2$
88.5	C_4H_5Cl	122.6	$C_5H_{11}OCl$	141.0	$C_4H_6OCl_2$
90.5	C_3H_3OCl	123.0	$C_4H_4Cl_2$	141.0	$C_5H_{10}Cl_2$
90.6	C_4H_7Cl	124.1	C_2OCl_4	142.5	$C_6H_3O_2Cl$
92.5	C_3H_5OCl	124.6	$C_4H_9O_2Cl$	142.6	C_7H_7OCl
92.6	C_4H_9Cl	125.0	$C_4H_6Cl_2$	143.0	$C_3H_4O_2Cl_2$
94.5	$C_2H_3O_2Cl$	126.6	C_7H_7Cl	143.0	$C_4H_8OCl_2$
94.5	C_3H_7OCl	126.9	$C_2O_2Cl_2$	144.6	$C_6H_5O_2Cl$
94.9	C_2Cl_2	127.0	$C_3H_4OCl_2$	144.6	$C_8H_{13}Cl$
97.0	$C_2H_2Cl_2$	127.0	$C_4H_8Cl_2$	145.4	$C_3H_3Cl_3$
98.9	$COCl_2$	128.6	C_6H_5OCl	146.6	$C_7H_{11}OCl$
99.0	$C_2H_4Cl_2$	128.6	C_7H_9Cl	146.7	$C_8H_{15}Cl$
102.6	C_5H_7Cl	128.9	$C_2H_2O_2Cl_2$	147.0	$C_6H_4Cl_2$
104.5	C_3HO_2Cl	129.0	$C_3H_6OCl_2$	147.4	C_2HOCl_3
104.5	C_4H_5OCl	130.5	$C_5H_3O_2Cl$	147.4	$C_3H_5Cl_3$
104.6	C_5H_9Cl	130.6	$C_7H_{11}Cl$	148.6	$C_6H_9O_2Cl$
106.5	$C_3H_3O_2Cl$	131.0	$C_2H_4O_2Cl_2$	148.6	$C_7H_{13}OCl$
106.6	C_4H_7OCl	131.4	C_2HCl_3	148.7	$C_8H_{17}Cl$
106.6	$C_5H_{11}Cl$	132.5	C_4HO_3Cl	149.0	$C_6H_6Cl_2$
108.5	$C_3H_5O_2Cl$	132.6	C_6H_9OCl	149.4	$C_2H_3OCl_3$
108.6	C_4H_9OCl	132.6	$C_7H_{13}Cl$	150.5	$C_4H_3O_4Cl$
110.5	$C_3H_7O_2Cl$	133.4	$C_2H_3Cl_3$	150.6	$C_5H_7O_3Cl$
111.0	$C_3H_4Cl_2$	134.6	$C_5H_7O_2Cl$	150.6	$C_6H_{11}O_2Cl$
112.6	C_6H_5Cl	134.6	$C_6H_{11}OCl$	150.7	$C_7H_{15}OCl$
112.9	$C_2H_2OCl_2$	134.7	$C_7H_{15}Cl$	151.0	$C_6H_8Cl_2$

IV. INDEX OF COMPOUNDS ACCORDING TO CHEMICAL TYPES

The numerous individual compounds of Order III whose preparation, properties, and reactions comprise the main text of this book are there listed in progressively increasing order of melting points (Division A, Solids), boiling points (Division B, Liquids), or empirical formulas (Division C, liquids for which data at ordinary pressure are not available). Unlike the treatment of Order I in an earlier volume, the compounds of the present Order III are not subdivided into genera. For this reason a highly useful feature of this volume is the following Chemical Type Index in which each compound is listed in one (or more) of the following eight arbitrary units.

UNIT 1. Chloro substitution products of saturated acyclic hydrocarbons.
UNIT 2. Chloro substitution products of unsaturated acyclic hydrocarbons
UNIT 3. Chloro substitution products of cyclic hydrocarbons.
UNIT 4. Chloro substitution products of hydroxy compounds.
UNIT 5. Chlorosubstitution products (and their relatives) of carbonyl compounds.
UNIT 6. Chloro substitution products of carboxylic acids and anhydrides.
UNIT 7. Acyl chlorides.
UNIT 8. Chlorine substitution products of ethers and of esters.

In order to facilitate recognition of the extent of subdivision of the above eight *units*, a brief summary of the subclassification is placed at the head of each one. Note that the names employed in this index are those best suited to recognition of the chemical relationships involved, and are not necessarily the same as those selected as principal names in the individual descriptions in the text.

Attention is also called to the fact that, in addition to this chemical type index, this volume is provided with conventional alphabetical name index and with empirical formula index.

UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF ACYCLIC SATURATED HYDROCARBONS

(Summary of Classification of Unit 1)

A. MONOCHLORO DERIVATIVES.
1. *With primary halogen.*
2. *With secondary halogen.*
3. *With tertiary halogen.*

M.W.	Formula
218.8	$C_{12}H_{23}OCl$
218.8	$C_{13}H_{27}Cl$
219.5	$C_6H_9O_2Cl_3$
219.9	$C_6H_6Cl_4$
220.8	$C_{12}H_{25}OCl$
221.0	$C_8H_6O_3Cl_2$
221.5	$C_5H_7O_3Cl_3$
221 5	$C_6H_{11}O_2Cl_3$
221.9	$C_4O_2Cl_4$
223.1	$C_{12}H_8Cl_2$
223.5	$C_8H_5OCl_3$
223.9	$C_4H_2O_2Cl_4$
224 0	$C_6H_{10}Cl_4$
225.1	$C_9H_{14}O_2Cl_2$
225.4	$C_7H_3O_2Cl_3$
225.5	$C_8H_7OCl_3$
225.9	$C_4H_4O_2Cl_4$
226 3	C_4HCl_5
226.7	$C_8H_{15}O_5Cl$
228.4	$C_4H_3Cl_5$
229.5	$C_6H_3O_3Cl_3$
230.0	$C_7H_4Cl_4$
230.3	C_3HOCl_5
230.4	$C_4H_5Cl_5$
230.7	$C_{14}H_{11}OCl$
231.5	$C_{10}H_5Cl_3$
231.9	$C_6H_2OCl_4$
232.8	$C_{13}H_{25}OCl$
232.8	$C_{14}H_{29}Cl$
233.5	$C_7H_{11}O_2Cl_3$
234.7	$C_{11}H_{19}O_3Cl$
235.0	$C_8H_4O_4Cl_2$
235.5	$C_6H_9O_3Cl_3$
236.8	C_2Cl_6
237.1	$C_{13}H_{10}Cl_2$
239.1	$C_{10}H_{16}O_2Cl_2$
239.9	$C_4H_2O_3Cl_4$
242.7	$C_{14}H_7O_2Cl$
243.1	$C_8H_{12}O_4Cl_2$
243.9	$C_7H_2OCl_4$
244.4	$C_5H_7Cl_5$
244.6	$C_9H_5O_6Cl$
244.7	$C_{14}H_9O_2Cl$
245.9	$C_6O_2Cl_4$
246.3	$C_3HO_2Cl_5$
246.7	$C_{14}H_{11}O_2Cl$
246.8	$C_{14}H_{27}OCl$
246 9	$C_{15}H_{31}Cl$
247.1	$C_{14}H_8Cl_2$
247.9	$C_6H_2O_2Cl_4$
248 8	C_3Cl_6
248.8	$C_{14}H_{29}OCl$
249.1	$C_{14}H_{10}Cl_2$
250.4	C_6HCl_5
250.8	$C_3H_2Cl_6$
251.1	$C_{13}H_8OCl_2$
251.2	$C_{14}H_{12}Cl_2$
255.5	$C_8H_5O_3Cl_3$
258.4	$C_6H_9Cl_5$
259.9	$C_7H_2O_2Cl_4$
260.8	C_4Cl_6
260.8	$C_{15}H_{29}OCl$
260.9	$C_{16}H_{33}Cl$
262.8	$C_4H_2Cl_6$
264.4	$C_7H_3Cl_5$
264.8	$C_4H_4Cl_6$
265.1	$C_{14}H_{10}OCl_2$
266 4	C_6HOCl_5
270.0	$C_{10}H_8Cl_4$
274.9	$C_{16}H_{31}OCl$
274.9	$C_{17}H_{35}Cl$
276.8	C_4OCl_6
276.9	$C_{16}H_{33}OCl$
278.4	C_7HOCl_5
278.8	$C_{19}H_{15}Cl$
280 8	$C_3O_2Cl_6$
281.1	$C_{14}H_{10}O_2Cl_2$
283.6	$C_{14}H_9Cl_3$
284.8	C_6Cl_6
285.2	C_3HCl_7
285.6	$C_{14}H_{11}Cl_3$
285.9	$C_8O_3Cl_4$
288.9	$C_{17}H_{33}OCl$
288.9	$C_{18}H_{37}Cl$
290.8	$C_6H_6Cl_6$
290.8	$C_{20}H_{15}Cl$
294 4	$C_7HO_2Cl_5$
296.8	$C_3O_3Cl_6$
298.8	$C_7H_2Cl_6$
299.3	$C_4H_3Cl_7$
300 8	C_6OCl_6
300.9	$C_{18}H_{33}OCl$
302.9	$C_{18}H_{35}OCl$
303 9	$C_8H_2O_4Cl_4$
304.9	$C_{18}H_{37}OCl$
308.8	$C_4O_3Cl_6$
312.8	C_7OCl_6
316.8	$C_6O_2Cl_6$
318.0	$C_{14}H_8Cl_4$
319.7	C_3Cl_8
319.7	$C_{12}H_{21}O_3Cl_3$
320.1	$C_{14}H_{10}Cl_4$
322.8	$C_5H_2O_3Cl_6$
333.3	C_7HCl_7
333.8	$C_4H_2Cl_8$
343.7	C_5Cl_8
349 8	$C_4H_2OCl_8$
354 5	$C_{14}H_9Cl_5$
388.9	$C_{14}H_8Cl_6$
403.8	$C_{10}Cl_8$
418.6	C_4OCl_{10}

2. *With secondary halogen*

3. *With tertiary halogen*

B DICHLORO DERIVATIVES.

1. *With both chlorine atoms primary.*
2.
   a. Both chlorine atoms on *same* carbon.
   b. Both chlorine atoms on *different* carbons.
3. *With both chlorine atoms tertiary.*
4. [illegible]
5.
6.

C TRICHLORO DERIVATIVES.

1. [illegible]
2.
3.
4.
5.
6.
7.

D. TETRACHLORO DERIVATIVES.

1. *With all four chlorine atoms primary.*
2. [illegible]
3.
4.
5.
6. *With two chlorine atoms primary, one secondary, and one tertiary.*

E. PENTACHLORO DERIVATIVES.

1. *With all five chlorine atoms primary*
2. *With four chlorine atoms primary and one secondary*
3. *With three chlorine atoms primary and two secondary.*
4. *With two chlorine atoms primary and three secondary*
5. *With four chlorine atoms primary and one tertiary*

F. HEXACHLORO DERIVATIVES

1. *With all six chlorine atoms primary*
2. *With five chlorine atoms primary and one secondary.*
3. *With four chlorine atoms primary and two secondary.*

G. HEPTACHLORO DERIVATIVES.

H. OCTACHLORO DERIVATIVES.

UNIT 1. CHLORO SUBSTITUTION PRODUCTS OF SATURATED ACYCLIC HYDROCARBONS

A. Monochloro Derivatives

1. *With primary halogen*

CH_3Cl	Methyl chloride	3:7005
C_2H_5Cl	Ethyl chloride	3:7015
C_3H_7Cl	*n*-Propyl chloride	3:7040
C_4H_9Cl	*n*-Butyl chloride	3:7160
	Isobutyl chloride	3:7135
$C_5H_{11}Cl$	*n*-Amyl chloride	3:7460
	sec.-Butylcarbinyl chloride	3:7345
$C_5H_{11}Cl$ Contd	Isoamyl chloride	3:7365
	Neopentyl chloride	3:7200
$C_6H_{13}Cl$	1-Chlorohexane	3:7955
	1-Chloro-2-methylpentane	3:7563
	5-Chloro-2-methylpentane	3:7695
	1-Chloro-3-methylpentane	3:0348
	1-Chloro-2-ethylbutane	3:7720

XII-630, XII_1-(313)] via diazotization (9) (6) and reaction with alc. (9), or by reduction to 3,4,5-trichlorophenylhydrazine and reaction of this with Fehling soln. (poor yield (6)) (5), see indic. refs.; for prepn. of $\bar{C}$ from 2,3-dichloroaniline [Beil. XII-621] (7) or from 2,6-dichloroaniline [Beil. XII-626] (7) (4) via diazotization and use of Cu_2Cl_2 reaction see indic. refs.; for prepn. of $\bar{C}$ from 4-chloro-3,5-diaminobenzenesulfonic acid-1 [Beil. XIV-718, XIV_1-(727)] via conv. to 3,4,5-trichlorobenzenesulfonic acid-1 and subsequently hydrolyzing the sulfonic acid group see (1).]

[For formn. of $\bar{C}$ (together with other prod.) from a mixt. of *o*- and *p*-dichlorobenzenes with Cl_2 (10), or from *m*-dichlorobenzene + $AlCl_3$ + Cl_2 (11), or from α-, β-, or γ-benzenehexachlorides with alc. KOH (5), or from α-benzenehexachloride with pyridine or quinoline (5), see indic. refs.]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg yields (9) exclusively 1,2,3,4-tetrachlorobenzene (3:0655), m.p. 44–45° (9); $\bar{C}$ with liq. Cl_2 in s.t. at room temp. for 7 days adds 6 atoms halogen yielding (12) 1,1′,2,2′,3,3′,4,5,6-enneachlorocyclohexane (1,2,3-trichlorobenzene hexachloride), pr. from MeOH, m.p. 80° (12).]

[$\bar{C}$ on hydrolysis with steam at 550–800° over cat. yields (13) pyrogallol (1:1555); for behavior of $\bar{C}$ with NaOMe in MeOH see (6) (14).]

$\bar{C}$ on mononitration, e.g., by soln. of $\bar{C}$ (1 g.) in 5 ml. fumg. HNO_3 ($D = 1.49$) (17), gives 100% yield (17) 1,2,3-trichloro-4-nitrobenzene [Beil. V-246], long colorless ndls. from alc., m.p. 56° (15) (7), 55–56° (17) (3) (note that the isomeric 1,2,3-trichloro-5-nitrobenzene [Beil. V-247, V_1-(131)] has m.p. 72°).

$\bar{C}$ on dinitration, e.g., $\bar{C}$ (1 g.) refluxed 1 hr. with 5 ml. fumg. HNO_3 ($D = 1.49$) + 5 ml. conc. H_2SO_4, then poured into aq. (17) (16), gives 100% yield 1,2,3-trichloro-4,6-dinitrobenzene, ndls. from hot alc., m.p. 92–93° (16) (17); this prod. (1 g). htd. 1 hr. at 100° with 5 g. aniline as directed (17) yields 1,3-dianilino-2-chloro-4,6-dinitrobenzene, cryst. from C_6H_6 or alc., m.p. 136–138° (17). [Note that an isomeric 1,2,3-trichloro-4,5-dinitrobenzene, cryst. from alc., m.p. 105–106° (16), has been obtd. by further nitration of 1,2,3-trichloro-5-nitrobenzene (mentioned in preceding paragraph).]

$\bar{C}$ with chlorosulfonic acid as directed (17) gives 1,2,3-trichlorobenzenesulfonyl chloride-4, m.p. 64–65° u.c. (17), 65–66° (2); this prod. with $(NH_4)_2CO_3$ readily yields (17) 1,2,3-trichlorobenzenesulfonamide-4, m.p. 226–230° dec. u.c. (17).

3:0990 (1) I.G., Brit. 319,149, Oct. 10, 1929; French 661,490, July 25, 1929; *Cent.* 1930, I 740. (2) I.G., Brit. 287,178, May 9, 1928; *Cent.* 1929, II 352. (3) Beilstein, Kurbatow, *Ann.* 192, 234–235 (1878). (4) Dadieu, Pongratz, Kohlrausch, *Monatsh.* 61, 431–432 (1932). (5) van der Linden, *Ber.* 45, 231–247 (1912). (6) Holleman, *Rec. trav. chim.* 37, 196–201 (1918). (7) Körner, Contardi, *Atti accad. Lincei* (5) 18, I 100 (1904). (8) Zünderwerke E. Brünn, A. G., Ger. 570,460, Feb. 16, 1933; *Cent.* 1933, I 2770. (9) Cohen, Hartley, *J. Chem. Soc.* 87, 1365–1366 (1905). (10) Britton (to Dow Chem. Co.), U.S. 1,923,419, Aug. 22, 1933; *Cent.* 1933, II 3049; *C.A.* 27, 5086 (1933).

(12) van der Linden, *Rec. trav. chim.*
March 15, 1932; *Cent.* 1932, I 2994;
779–780 (1931). (15) Holleman,
(1921). (17) Hunt

B. Dichloro Derivatives

1. *With both chlorine atoms* primary

a. Both chlorine atoms on *same* carbon

b. The two chlorine atoms on *different* carbons

2. *With both chlorine atoms* secondary

a. Both chlorine atoms on *same* carbon

$C_3H_6Cl_2$	2,2-Dichloropropane..	**3:7140**
$C_4H_8Cl_2$	2,2-Dichlorobutane...	**3:7415**
$C_5H_{10}Cl_2$	2,2-Dichloropentane..	**3:7755**
	3,3-Dichloropentane..	**3:7895**
	3,3-Dichloro-2-methylbutane......	**3:9230**
$C_6H_{12}Cl_2$	2,2-Dichlorohexane...	**3:9342**
	3,3-Dichloro-2,2-dimethylbutane. ..	**3:4325**
	4,4-Dichloro-2,2-dimethylbutane .	**3:8132**
$C_7H_{14}Cl_2$	2,2-Dichloroheptane..	**3:9424**
	4,4-Dichloroheptane .	**3:9426**
	3,3-Dichloro-2,4-dimethylpentane.....	**3:7610**
$C_8H_{16}Cl_2$	2,2-Dichloro-octane...	**3:8670**
	3,3-Dichloro-2,2,4-trimethylpentane ..	**3:9536**

b. Both chlorine atoms on *different* carbons

$C_4H_8Cl_2$	*d,l*-2,3-Dichlorobutane	**3:7615**
	meso-2,3-Dichlorobutane	**3:7580**
$C_5H_{10}Cl_2$	2,3-Dichloropentane..	**3:8010**
	2,4-Dichloropentane.	**3:8120**
$C_6H_{12}Cl_2$	2,3-Dichlorohexane	**3:8300**
	2,5-Dichlorohexane. .	**3:8525**
	3,4-Dichlorohexane...	**3:9344**

3. *With both chlorine atoms* tertiary

$C_6H_{12}Cl_2$	2,3-Dichloro-2,3-dimethylbutane. ..	**3:4520**
$C_7H_{14}Cl_2$	2,4-Dichloro-2,4-dimethylpentane ..	**3:9428**
$C_8H_{16}Cl_2$	2,5-Dichloro-2,5-dimethylhexane....	**3:1550**
	3,4-Dichloro-3,4-dimethylhexane....	**3:8315**
$C_9H_{18}Cl_2$	2,6-Dichloro-2,6-dimethylheptane...	**3:0455**
$C_{10}H_{20}Cl_2$	2,7-Dichloro-2,7-dimethyloctane....	**3:0840**
	3,4-Dichloro-3,4-dimethylhexane....	**3:9724**

4. *With one chlorine* primary *and one* secondary

$C_3H_6Cl_2$	1,2-Dichloropropane..	**3:5200**
$C_4H_8Cl_2$	1,2-Dichlorobutane...	**3:7680**
	1,3-Dichlorobutane...	**3:7925**
$C_5H_{10}Cl_2$	1,2-Dichloropentane..	**3:8140**
	1,3-Dichloropentane..	**3:9220**
	1,4-Dichloropentane..	**3:9224**
	1,3-Dichloro-2-methylbutane	**3:9228**
	3,4-Dichloro-2-methylbutane...........	**3:8075**
$C_6H_{12}Cl_2$	1,2-Dichlorohexane ..	**3:8380**
	1,5-Dichlorohexane...	**3:9340**
$C_7H_{14}Cl_2$	1,2-Dichloroheptane..	**3:9420**
	1,2-Dichloro-4,4-dimethylpentane...	**3:8516**
$C_8H_{16}Cl_2$	1,6-Dichloro-octane...	**3:9530**
	1,7-Dichloro-octane...	**3:9532**
	4-Chloro-3-(chloromethyl)heptane.. .	**3:9534**
$C_9H_{18}Cl_2$	1,2-Dichlorononane...	**3:9632**

5. *With one chlorine* primary *and one* tertiary

$C_4H_8Cl_2$	1,2-Dichloro-2-methylpropane.....	**3:7430**
$C_5H_{10}Cl_2$	1,2-Dichloro-2-methylbutane......	**3:7920**
	2,4-Dichloro-2-methylbutane......	**3:8105**
$C_6H_{12}Cl_2$	2,5-Dichloro-2-methylpentane.....	**3:8540**

6. *With one chlorine* secondary *and one* tertiary

$C_5H_{10}Cl_2$	2,3-Dichloro-2-methylbutane......	**3:7975**
$C_6H_{12}Cl_2$	2,3-Dichloro-2-methylpentane.....	**3:9346**

C. Trichloro Derivatives

1. *With all three chlorine atoms* primary

$CHCl_3$	Chloroform........ .	**3:5050**

$C_6H_{11}Cl$	2-Chlorohexene-1	3:7530
	3-Chlorohexene-3.....	3:7535
	2-Chloro-3,3-dimethylbutene-1..........	3:7340
$C_7H_{13}Cl$	2-Chloroheptene-1....	3:7988
	4-Chloroheptene-3....	3:8023
	3-Chloro-2,4-dimethylpentene-2.........	3:7605
$C_8H_{15}Cl$	2-Chloro-octene-1 ...	3:8346
	2-Chloro-octene-2	3:8345
	4-Chloro-octene-4 .. .	3:8230
	2-Chloro-3-ethyl-3-methylpentene-1...	3:8115
$C_{10}H_{19}Cl$	5-Chlorodecene-5.....	3:9712

b_2 DICHLORO

$C_3H_4Cl_2$	2,3-Dichloropropene-1	3:5190
$C_4H_6Cl_2$	2,3-Dichlorobutene-1 .	3:9074
	1,2-Dichlorobutene-2 (h.-b.)......	3:5615
	1,2-Dichlorobutene-2 (l.-b.)	3:5360
	1,3-Dichlorobutene-2 .	3:5550
$C_5H_8Cl_2$	2,5-Dichloropentene-2	3:9202
	3,4-Dichloropentene-2	3:8045
	1,3-Dichloro-2-methylbutene-2..........	3:8170

b_3 POLYCHLORO

$C_4H_5Cl_3$	1,2,4-Trichlorobutene-2....	3:9062
	2,3,4-Trichlorobutene-2.....	3:9064
$C_4H_4Cl_4$	2,3,3,4-Tetrachlorobutene-1..........	3:9060

2. *With two chlorine atoms on* C *attached to unsaturation*

a. Both these chlorines are on same C atom

$C_2H_2Cl_2$	1,1-Dichloroethylene..	3:5005
$C_3H_4Cl_2$	1,1-Dichloropropene-1	3:5120
$C_4H_6Cl_2$	1,1-Dichloro-2-methylpropene-1.........	3:5300
C_2HCl_3	1,1,2-Trichloroethylene..........	3:5170
$C_3H_3Cl_3$	1,1,2-Trichloropropene-1.........	3:5395
$C_4H_5Cl_3$	1,1,3-Trichloro-2-methylpropene-1...	3:5025
$C_6H_9Cl_3$	1,1,2-Trichlorohexene-1.........	3:9326
C_2Cl_4	Tetrachloroethylene ..	3:5460
C_3HCl_5	1,1,2,3,3-Pentachloropropene-1.........	3:6075
C_3Cl_6	Hexachloropropene...	3:6370

These two chlorines are on different carbons

$(-\underset{Cl}{\underset{\mid}{C}}=\underset{Cl}{\underset{\mid}{C}}-)$

$C_2H_2Cl_2$	*cis*-1,2-Dichloroethylene	3:5042
	trans-1,2-Dichloroethylene..........	3:5028
$C_3H_4Cl_2$	1,2-Dichloropropene-1 (h.-b. isomer)	3:5150
	1,2-Dichloropropene-1 (l.-b. isomer)......	3:5110
	cis-2,3-Dichlorobutene-2..........	3:5500
	trans-2,3-Dichlorobutene-2	3:7395
$C_6H_{10}Cl_2$	1,2-Dichlorohexene-1 .	3:9330
C_2HCl_3	1,1,2-Trichloroethylene.........	3:5170
$C_3H_3Cl_3$	1,1,2-Trichloropropene-1.	3:5395
	1,2,3-Trichloropropene-1............	3:5050
$C_3H_2Cl_4$	1,2,3,3-Tetrachloropropene-1.........	3:5920
C_2Cl_4	Tetrachloroethylene ..	3:5460
$C_4H_2Cl_6$	1,1,2,3,4,4-Hexachlorobutene-2	
	(liquid isomer).......	3:9046
	(solid isomer)........	3:1945
$C_6H_6Cl_6$	1,2,3,4,5,6-Hexachlorohexene-3.....	3:1220

b. Dichloro

C_2Cl_2	Dichloroacetylene....	**3:5010**

2. ***With chlorine(s) attached to some* C *other than that bearing triple bond***

a. Monochloro

a_1 CHLORINE IS PRIMARY

C_3H_3Cl	3-Chloropropyne-1....	**3:7100**
C_4H_5Cl	1-Chlorobutyne-2.....	**3:7175**
$C_8H_{13}Cl$	1-Chloro-octyne-2....	**3:9514**

a_2 CHLORINE IS TERTIARY

C_5H_7Cl	3-Chloro-3-methylbutyne-1........	**3:7155**
C_6H_9Cl	3-Chloro-3-methylpentyne-1..	**3:9322**
	4-Chloro-4-methylpentyne-2.......	**3:9324**
$C_8H_{13}Cl$	3-Chloro-3-methylheptyne-4.........	**3:9516**
$C_9H_{15}Cl$	2-Chloro-2-methyloctyne-3..........	**3:9622**
$C_{10}H_{17}Cl$	3-Chloro-3-methylnonyne-4.	**3:9710**

b. Dichloro

$C_8H_{12}Cl_2$	2,5-Dichloro-2,5-dimethylhexene-3 ..	**3:9504**

F. Of Alkadi-ynes

C_4Cl_2	1,4-Dichlorobuta-di-yne-1,3.........	**3:9040**

G. Of Alkenynes

C_4H_3Cl	1-Chlorobuten-3-yne-1	**3:7070**
C_7H_9Cl	5-Chloro-5-methylhexen-1-yne-3 ..	**3:9402**

UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI

(Summary of Classification of Unit 3)

A. Of Cycloalkanes.
B. Of Mononuclear Aromatic Hydrocarbons.
  1. *With all chlorine in nucleus.*
  2. *With all chlorine in side chain(s).*
    a. Saturated side chain(s).
    b. Unsaturated side chain(s).
  3. *With chlorine both in ring and in side chain(s).*
C. Of Polynuclear Aromatic Hydrocarbons.
  1. *With all chlorine in nucleus.*
    a. Systems with uncondensed rings.
    b. Systems with condensed rings.
  2. *With all chlorine in side chain(s).*
    a. Systems with two uncondensed rings.
    b. Systems with two condensed rings.
    c. Systems with three uncondensed rings.
  3. *With chlorine both in nucleus and side chain.*

UNIT 3. CHLORO SUBSTITUTION PRODUCTS OF HYDROCARBONS CONTAINING CYCLIC NUCLEI

A. Of Cycloalkanes

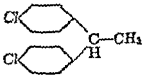
C_5H_9Cl	Chlorocyclopentane...	**3:7545**
$C_6H_{11}Cl$	Chlorocyclohexane....	**3:8040**
$C_6H_6Cl_6$	*cis*-1,2,3,4,5,6-Hexachlorocyclohexane..	**3:4410**
	trans-1,2,3,4,5,6-Hexachlorocyclohexane..	**3:4990**

B. Of Mononuclear Aromatic Hydrocarbons

1. ***With all chlorine in nucleus***

C_6H_5Cl	Chlorobenzene.......	**3:7903**
$C_6H_4Cl_2$	*o*-Dichlorobenzene ...	**3:6055**
	m-Dichlorobenzene...	**3:5960**
	p-Dichlorobenzene....	**3:0980**

3:0995 1,1-Di-(*p*-CHLOROPHENYL)ETHANE $C_{14}H_{12}Cl_2$ **Beil. S.N. 470**



M.P. 54–55° (1) **B.P. 143–145° at 2 mm. (1)**

Colorless cryst. from 90% AcOH. — Note that, when pure, neither solid Č nor its solns. show any fluorescence either in visible or ultraviolet light. (1). — Note also that, although m.p. of Č is identical with that of its next lower homolog, viz., di-(*p*-chlorophenyl)methane (4,4'-dichlorodiphenylmethane) (3:1057), nevertheless the m.p. of their mixture is depressed to 40–50° (1).

[For prepn. of Č from 1,1-di-(*p*-chlorophenyl)ethylene (3:2475) by cat. hydrogenation (62% yield) see (1); for formn. of Č from chlorobenzene (3:7903) with acetylene in presence of $AlCl_3$ see (2), but note that by this method various undetermined impurities which show blue fluorescence are also formed (1).]

Č on oxidn. with CrO_3/AcOH + trace of H_2SO_4 gives (1) 4,4'-dichlorobenzophenone (3:4270), m.p. 142–144°.

Č does *not* (1) yield an addn. prod. with PkOH.

3:0995 (1) Grummitt, Buck, Becker, *J. Am. Chem. Soc.* **67**, 2265–2266 (1945). (2) Cook, Chambers, *J. Am. Chem. Soc.* **43**, 338 (1921).

UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

A. Of Alcohols

1. *Of acyclic alcohols*

a. Saturated monohydric

a₁ PRIMARY

C_2H_5OCl	2-Chloroethanol-1	**3:5552**
$C_2H_4OCl_2$	2,2-Dichloroethanol-1	**3:5745**
$C_2H_3OCl_3$	2,2,2-Trichloroethanol-1	**3:5775**
C_3H_7OCl	2-Chloropropanol-1	**3:7917**
	3-Chloropropanol-1	**3:8285**
$C_3H_6OCl_2$	2,3-Dichloropropanol-1	**3:6060**
C_4H_9OCl	2-Chlorobutanol-1	**3:9160**
	3-Chlorobutanol-1	**3:9165**
	4-Chlorobutanol-1	**3:9170**
$C_4H_7OCl_3$	2,2,3-Trichlorobutanol-1	**3:1336**
C_4H_9OCl	2-Chloro-2-methylpropanol-1	**3:7905**
	3-Chloro-2-methylpropanol-1	**3:9180**
$C_5H_{11}OCl$	5-Chloropentanol-1	**3:9295**
$C_6H_{13}OCl$	6-Chlorohexanol-1	**3:9395**
$C_7H_{15}OCl$	7-Chloroheptanol-1	**3:0013**
$C_8H_{17}OCl$	8-Chloro-octanol-1	**3:9590**
$C_9H_{19}OCl$	9-Chlorononanol-1	**3:0170**
$C_{10}H_{21}OCl$	10-Chlorodecanol-1	**3:0014**
$C_{12}H_{25}OCl$	12-Chlorododecanol-1	**3:0172**
$C_{14}H_{29}OCl$	14-Chlorotetradecanol-1	**3:0375**
$C_{16}H_{33}OCl$	16-Chlorohexadecanol-1	**3:0525**
$C_{18}H_{37}OCl$	18-Chloro-octadecanol-1	**3:0985**

a₂ SECONDARY

C_3H_7OCl	1-Chloropropanol-2	**3:7747**
$C_3H_6OCl_2$	1,1-Dichloropropanol-2	**3:5755**
	1,3-Dichloropropanol-2	**3:5985**
$C_3H_5OCl_3$	1,1,1-Trichloropropanol-2	**3:0846**
$C_3H_4OCl_4$	1,1,1,3-Tetrachloropropanol-2	**3:9036**
	1,1,3,3-Tetrachloropropanol-2	**3:9037**
C_4H_9OCl	1-Chlorobutanol-2	**3:8025**
	3-Chlorobutanol-2	**3:8000**
	erythro-3-Chlorobutanol-2	**3:8004**
	threo-3-Chlorobutanol-2	**3:8002**
	4-Chlorobutanol-2	**3:9175**
$C_4H_8OCl_2$	1,3-Dichlorobutanol-2	**3:9145**
	1,1-Dichloro-2-methylpropanol-2	**3:5772**
$C_4H_7OCl_3$	1,1,1-Trichlorobutanol-2	**3:5955**
$C_5H_{11}OCl$	1-Chloropentanol-2	**3:8225**
	1-Chloropentanol-3	**3:8500**
	2-Chloro-2-methylbutanol-3	**3:9290**

a₃ TERTIARY

C_4H_9OCl	1-Chloro-2-methylpropanol-2	**3:7752**
$C_4H_8OCl_2$	1,3-Dichloro-2-methylpropanol-2	**3:5977**
$C_4H_7OCl_3$	1,1,1-Trichloro-2-methylpropanol-2	**3:2662**
$C_5H_{11}OCl$	1-Chloro-2-methylbutanol-2	**3:8175**
	3-Chloro-2-methylbutanol-2	**3:8030**
	4-Chloro-2-methylbutanol-2	**3:8335**

b. Saturated dihydric

$C_3H_7O_2Cl$	3-Chloropropanediol-1,2	**3:9038**
	2-Chloropropanediol-1,3	**3:9039**
$C_4H_9O_2Cl$	3-Chloro-2-methylpropanediol-1,2	**3:9190**

c. Unsaturated (olefinic) monohydric

c₁ PRIMARY

C_3H_5OCl	2-Chloropropen-2-ol-1	**3:5635**
	3-Chloropropen-2-ol-1	**3:5820**

UNIT 4. CHLORO SUBSTITUTION PRODUCTS OF HYDROXY COMPOUNDS

(Summary of Classification of Unit 4)

A. Of Alcohols
- 1. *Of acyclic alcohols.*
  - *a.* Saturated monohydric.
    - a_1 Primary.
    - a_2 Secondary.
    - a_3 Tertiary.
  - *b.* Saturated dihydric.
  - *c.* Unsaturated (olefinic) monohydric.
    - c_1 Primary.
    - c_2 Secondary.
- 2. *Of cyclanols (alicyclic alcohols).*
- 3. *Of aromatic alcohols.*
- 4. *Of alcohols containing also other functional groups.*
  - *a.* Ether/alcohols.
  - *b.* Ester/alcohols.
  - *c.* Ether/ester/alcohols.
  - *d.* Acid/alcohols (hydroxy acids).

B. Of Phenols.
- 1. *Of mononuclear phenols.*
  - *a.* Monohydric.
    - a_1 Derivatives of phenol.
    - a_2 Derivatives of methylphenols.
    - a_3 Derivatives of xylenols.
    - a_4 Derivatives of miscellaneous alkylphenols.
    - a_5 Derivatives of phenolic aldehydes.
    - a_6 Derivatives of phenolic acids.
    - a_7 Derivatives of phenolic acid chlorides.
  - *b.* Dihydric.
    - b_1 Derivatives of pyrocatechol.
    - b_2 Derivatives of resorcinol.
    - b_3 Derivatives of hydroquinone.
  - *c.* Trihydric.
- 2. *Of binuclear phenols.*
  - *a.* Monohydric.
    - a_1 With uncondensed rings.
    - a_2 With condensed rings.

UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

(Summary of Classification of Unit 5)

A. Of Aldehydes.
- 1. *Acyclic aldehydes.*
  - *a.* Saturated.
  - *b.* Unsaturated.
  - *c.* Relatives of the above.
    - c_1 Hydrates.
    - c_2 Hemiacetals.
    - c_3 Diethylacetals.
    - c_4 Acetals with chlorine only in alcohol radicals;
    - c_5 Polymers.
- 2. *Aromatic aldehydes.*
  - *a.* Simple aldehydes.
  - *b.* Phenolic aldehydes.

B. Of Ketones.
- 1. *Dialkyl ketones.*
- 2. *Alicyclic ketones.*
- 3. *Alkyl aryl ketones.*
  - *a.* With chlorine only in alkyl.
  - *b.* With chlorine both in alkyl and aryl.
  - *c.* With chlorine only in aryl.
- 4. *Diaryl ketones.*
- 5. *Ketones containing also other functional groups.*
  - *a.* Keto-acid chlorides.
  - *b.* Keto-acid esters.

C. Of Quinones.
- 1. *Mononuclear quinones.*
- 2. *Dinuclear quinones.*
- 3. *Trinuclear quinones.*

UNIT 5. CHLORO SUBSTITUTION PRODUCTS OF CARBONYL COMPOUNDS (AND THEIR RELATIVES)

A. Of Aldehydes

1. *Acyclic Aldehydes*

a. Saturated

C_2H_3OCl	Chloroacetaldehyde...	**3:7212**
$C_2H_2OCl_2$	Dichloroacetaldehyde.	**3:5180**
C_2HOCl_3	Trichloroacetaldehyde	**3:5210**
C_3H_5OCl	α-Chloropropionaldehyde...........	**3:5160**
	β-Chloropropionaldehyde..............	**3:5576**
$C_3H_4OCl_2$	α,α-Dichloropropionaldehyde.........	**3:9033-A**
	α,β-Dichloropropionaldehyde..........	**3:9034**
$C_3H_3OCl_3$	α,α,β-Trichloropropionaldehyde......	**3:9033**
C_4H_7OCl	α-Chloro-*n*-butyraldehyde.....	**3:9109**
	β-Chloro-*n*-butyraldehyde.....	**3:9110**
	γ-Chloro-*n*-butyraldehyde.....	**3:9111**
$C_4H_6OCl_2$	α,β-Dichloro-*n*-butyraldehyde.....	**3:9103**
$C_4H_5OCl_3$	α,α,β-Trichloro-*n*-butyraldehyde.....	**3:5910**
	α,α,γ-Trichloro-*n*-butyraldehyde.....	**3:9094**
C_4H_7OCl	α-Chloro-iso-butyraldehyde.....	**3:7235**
	β-Chloro-iso-butyraldehyde.....	**3:9112**

B. Of Isocyclic Acids.
  1. *With no other functional group.*
    a. Monobasic.
    b. Dibasic.
    c. Tribasic.
  2. *With some other functional group.*
    a. Phenolic acids.
    b. Ether acids.

C. Anhydrides of Acyclic Acids.
  1. Saturated.
  2. Unsaturated.

D. Anhydrides of Isocyclic Acids.

UNIT 6. CHLORO SUBSTITUTION PRODUCTS OF CARBOXYLIC ACIDS AND ANHYDRIDES

(For acyl chlorides see Unit 7)

A. *Of Acyclic Acids*
  1. *With no other functional group*
    a. Saturated monobasic

$C_2H_3O_2Cl$	Chloroacetic acid	3:1370
$C_2H_2O_2Cl_2$	Dichloroacetic acid	3:6208
$C_2HO_2Cl_3$	Trichloroacetic acid	3:1150
$C_3H_5O_2Cl$	α-Chloropropionic acid	3:6125
	β-Chloropropionic acid	3:0460
$C_3H_4O_2Cl_2$	α,α-Dichloropropionic acid	3:6162
	α,β-Dichloropropionic acid	3:0855
	β,β-Dichloropropionic acid	3:1058
$C_3H_3O_2Cl_3$	α,α,β-Trichloropropionic acid	3:1275
$C_3H_2O_2Cl_4$	α,α,β,β-Tetrachloropropionic acid	3:1850
$C_3HO_2Cl_5$	Pentachloropropionic acid	3:4895
$C_4H_7O_2Cl$	α-Chloro-*n*-butyric acid	3:9130
	β-Chloro-*n*-butyric acid	3:0035
	γ-Chloro-*n*-butyric acid	3:0020
$C_4H_6O_2Cl_2$	α,β-Dichloro-*n*-butyric acid	
	Higher-melting isomer	3:1903
	Lower-melting isomer	3:1375
$C_4H_5O_2Cl_3$	α,α,β-Trichloro-*n*-butyric acid	3:1280
$C_4H_5O_2Cl_3$ Contd.	α,α,γ-Trichloro-*n*-butyric acid	3:1831
	α,β,β-Trichloro-*n*-butryic acid	3:0925
	γ,γ,γ-Trichloro-*n*-butryic acid	3:1000
$C_4H_7O_2Cl$	α-Chloroisobutyric acid	3:0235
	β-Chloroisobutyric acid	3:9132
$C_5H_9O_2Cl$	α-Chloro-*n*-valeric acid	3:8783
	β-Chloro-*n*-valeric acid	3:0270
	γ-Chloro-*n*-valeric acid	3:9270
	δ-Chloro-*n*-valeric acid	3:0075
	α-Chloro-α-methyl-*n*-butyric acid	3:8718
	α-Chloro-β-methyl-*n*-butyric acid	3:0050
	β-Chloro-α,α-dimethyl-propionic acid	3:0440

b. Saturated dibasic

$C_4H_4O_4Cl_2$	*d,l*-α,α′-Dichlorosuccinic acid	3:4711
	meso-α,α′-Dichlorosuccinic acid	3:4930

c. Unsaturated (olefinic) monobasic

$C_3H_3O_2Cl$	α-Chloroacrylic acid	3:1445
	β-Chloroacrylic acid	3:2240
$C_3H_2O_2Cl_2$	α,β-Dichloroacrylic acid	3:2265
	β,β-Dichloroacrylic acid	3:1875
$C_3HO_2Cl_3$	α,β,β-Trichloroacrylic acid	3:1840

UNIT 6. CHLORO SUBSTITUTION PRODUCTS OF CARBOXYLIC ACIDS AND ANHYDRIDES

(Summary of Classification of Unit 6)

A. Of Acyclic Acids.

1. *With no other functional group.*
   - *a.* Saturated monobasic.
   - *b.* Saturated dibasic.
   - *c.* Unsaturated (olefinic) monobasic.
   - *d.* Unsaturated (olefinic) dibasic.
   - *e.* Unsaturated (acetylenic) monobasic.
2. *With some other functional group.*
   - *a.* Hydroxy monobasic.

CHAPTER IV

DIVISION A. SOLIDS

(3:1000–3:1499)

3:1000 γ,γ,γ-TRICHLORO-*n*-BUTYRIC ACID $C_4H_5O_2Cl_3$ Beil. S.N. 162
$Cl_3C.CH_2.CH_2.COOH$

M.P. 55° (1)

Colorless ndls. from hot aq.

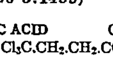
[For prepn. of $\bar{C}$ from γ,γ,γ-trichloro-*n*-butyronitrile (see below) by hydrolysis with conc. HCl at 60° for 6 hrs. see (1).]

——γ,γ,γ-Trichloro-*n*-butyronitrile: ndls. from pet. ether, m.p. 41° u.c.; b.p. 214–216° at 760 mm., 90–95° at 12 mm. (1). [From acrylonitrile with $CHCl_3$ in pres. of aq. trimethylbenzylammonium hydroxide at 0.5° for 24 hrs. (11% yield (1)).] [Note that this nitrile upon acid hydrolysis gives $\bar{C}$, but upon alkaline hydrolysis gives succinic acid (1:0530), m.p. 188–189° (1).]

——γ,γ,γ-Trichloro-*n*-butyramide: cryst. from toluene, m.p. 89–90° u.c. (1). [From γ,γ,γ-trichloro-*n*-butyronitrile (above) with 27% H_2O_2 + aq. NaOH at 40–45° for 5 hrs. (1).]

3:1000 (1) Bruson, Niederhauser, Riener, Hester, *J. Am. Chem. Soc.* **67**, 601 (1945).

3:1010 3-CHLORO-2-HYDROXYBENZALDE-HYDE $C_7H_5O_2Cl$ Beil. VIII — VIII$_1$-(523)
(3-Chlorosalicylaldehyde)



M.P. 55° (1)
54.5–55.5° (2)
54° (3) (4)

Long colorless ndls. from MeOH (1). — Readily sol. in usual org. solvents (1). — Volatile with steam [diff. from 3-chloro-4-hydroxybenzaldehyde (3:4065) (1)].

[For prepn. from *o*-chlorophenol (3:5980) with $CHCl_3$ + alk. (10–15% yield (1)) or via condensation with formalin + alk. to 3-chloro-2-hydroxybenzyl alc. and oxidn. of latter with Na *m*-nitrobenzenesulfonate + alk. (2) see indic. refs.; from 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic ac.) (3:4745) by reductn. with Na/Hg in pres. of H_3BO_3 see (4).]

$\bar{C}$ with satd. aq. $NaHSO_3$ soln. yields $NaHSO_3$ cpd. (1) (2).

$\bar{C}$ dissolves in aq. alk. with yel. color (4) (2).

$\bar{C}$ with aq. $FeCl_3$ yields violet-red color (2).

$\bar{C}$ is not nitrated by cold AcOH/HNO_3 soln. (1); but $\bar{C}$ (2 g.) in AcOH (10 ml.) treated at 45° for 15 min. with soln. of 0.8 ml. conc. HNO_3 ($D = 1.42$) in AcOH (4 ml.), then poured into aq., gives (1) 2.15 g. 3-chloro-5-nitro-2-hydroxybenzaldehyde, yel. ndls. from dil. alc., m.p. 129° (1).

The methyl ether of $\bar{C}$, viz., 3-chloro-2-methoxybenzaldehyde, is a liq., b.p. abt. 255°, f.p. 0° (1).

UNIT 7. ACYL CHLORIDES

(Summary of Classification of Unit 7)

A. Of Acyclic Acids (R.CO.Cl).

1. *The radical (R) contains no chlorine.*
   - *a.* Corresponding acid is saturated and monobasic.
   - *b.* Corresponding acid is saturated and dibasic.
   - *c.* Corresponding acid is unsaturated and monobasic.
   - *d.* Corresponding acid is unsaturated and dibasic.
   - *e.* Corresponding acid contains also other functional groups.
     - e_1 Ether/acyl chloride.
     - e_2 Ester/acyl chloride.
     - e_3 Keto/acyl chloride.
2. *The radical (R) does contain chlorine.*
   - *a.* Corresponding acid is saturated and monobasic.
   - *b.* Corresponding acid is saturated and dibasic.
   - *c.* Corresponding acid is unsaturated and monobasic.
   - *d.* Corresponding acid is unsaturated and dibasic.
   - *e.* Corresponding acid contains other functional groups.

B. Of Isocyclic Acids.

1. *The radical (R) contains no chlorine.*
   - *a.* Corresponding acid is monobasic.
     - a_1 With —COOH group attached to ring.
     - a_2 With —COOH group attached to saturated side chain.
     - a_3 With —COOH group attached to unsaturated side chain.
     - a_4 With —COOH group attached to ring containing another functional group.
   - *b.* Corresponding acid is dibasic.
2. *The radical (R) does contain chlorine.*
   - *a.* Corresponding acid is monobasic.

C. Of Heterocyclic Acids.

1. *The radical (R) contains no chlorine.*
   - *a.* Corresponding acid is monobasic.

UNIT 7. ACYL CHLORIDES

A. Of Acyclic Acids (R.CO.OH)

1. *The radical (R) contains no chlorine*

a. Corresponding acid is saturated and monobasic

C_2H_3OCl	Acetyl chloride	3:7065
C_3H_5OCl	Propionyl chloride....	3:7170
C_4H_7OCl	*n*-Butyryl chloride ...	3:7370
	Isobutyryl chloride...	3:7270
C_5H_9OCl	*n*-Valeryl chloride....	3:7740
	α-Methyl-*n*-butyryl chloride...........	3:7603
	β-Methyl-*n*-butyryl chloride...........	3:7560
	α,α-Dimethylpropionyl chloride...........	3:7450
$C_6H_{11}OCl$	*n*-Caproyl chloride....	3:8163
	α-Methyl-*n*-valeryl chloride...........	3:8020
	β-Methyl-*n*-valeryl chloride....... ...	3:8035
	γ-Methyl-*n*-valeryl chloride...........	3:8090
	α-Ethyl-*n*-butyryl chloride...........	3:7930
	α,α-Dimethyl-*n*-butyryl chloride....	3:7900
	α,β-Dimethyl-*n*-butyryl chloride....	3:7965
	β,β-Dimethyl-*n*-butyryl chloride.....	3:7890
$C_7H_{13}OCl$	*n*-Heptanoyl chloride .	3:8530

UNIT 8. CHLORO SUBSTITUTION PRODUCTS OF ETHERS AND OF ESTERS

(Summary of Classification of Unit 8)

A. Ethers.
- 1. *Completely acyclic saturated ethers.*
  - *a.* Monoethers.
    - a_1 Derived from symmetrical ethers.
    - a_2 Derived from unsymmetrical ethers.
  - *b.* Diethers.
  - *c.* Ethers containing also other functions.
    - c_1 Ether/alcohols.
    - c_2 Ether/esters.
    - c_3 Ether/ester/alcohols.
    - c_4 Ether/ester/acyl halides.
- 2. *Completely acyclic unsaturated ethers.*
- 3. *Cyclic ethers.*
  - *a.* Non-aromatic.
    - a_1 Monoethers.
    - a_2 Diethers.
  - b. Aromatic ethers (phenol ethers).
  - *c.* Heterocyclic ethers.

B. Esters.
- 1. *Esters of aliphatic acids.*
  - *a.* Acids containing no chlorine.
    - a_1 From acetic acid.
    - a_2 From oxalic acid.
    - a_3 From carbonic acid.
  - *b.* Saturated monobasic acids containing chlorine.
    - b_1 From chloroacetic acid.
    - b_2 From dichloroacetic acid.
    - b_3 From trichloroacetic acid.

Ⓓ 3-Chloro-2-hydroxybenzaldoxime: *lfts. from dil. alc., m.p. 167–168° (2).*

—— 3-Chloro-2-hydroxybenzaldehyde phenylhydrazone: unrecorded.

—— 3-Chloro-2-hydroxybenzaldehyde *p*-nitrophenylhydrazone: unrecorded.

—— 3-Chloro-2-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

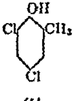
Ⓓ 3-Chloro-2-hydroxybenzaldehyde semicarbazone: cryst. from 50% AcOH, m.p. 240–243° (2).

3:1010 (1) Davies, Rubinstein, *J. Chem. Soc.* **123**, 2850 (1923). (2) Hanus, *J. prakt. Chem.* (2) **158**, 263–264 (1941). (3) Duff, *J. Chem. Soc.* **1941**, 547–550. (4) Bayer and Co., Ger. 228,838, Nov. 22, 1910; *Cent.* **1911**, I 51.

3:1020 4,6-DICHLORO-2-METHYLPHENOL $C_7H_6OCl_2$ Beil. VI - 359

(4,6-Dichloro-*o*-cresol) VI_1-(174)

VI_2-(332)



M.P. 56°	(1)	B.P. 220.5°		(1)
55°	(2) (7)	131°	at 28 mm.	(5)
54–55°	(3)	73–78°	at 4 mm.	(6)
54° u.c.	(4)			
53–54°	(5)			

Ndls. from hot aq. or pet. ether. Spar. sol. cold but more eas. sol. hot aq.; eas. sol. alc., ether, $CHCl_3$, CS_2. Volatile with steam.

[For prepn. of $\bar{C}$ from *o*-cresol (1:1400) with Cl_2 (7) (4) (1) in CCl_4 (61% yield (2)) in CCl_4 in pres. of Fe (8) or in pres. of PCl_3 in sunlight at elevated temp. (8), with Cl_2 in NaOH soln. at room temp. (5), or with SO_2Cl_2 (3), see indic. refs; for formn. from 2-methylphenoldisulfonic acid-4,6 (6) in nitrobenzene with Cl_2 (other products are also formed) see (6).]

[$\bar{C}$ with dry NH_3 gas at room temp. (9) forms a cpd., $\bar{C}.2NH_3$ (9); $\bar{C}$ on evapn. of alc. NH_3 soln. does *not* give an NH_4 salt but is recovered unchanged (dif. from 2,6-dichloro-4-methylphenol (3:0400) *q.v.*) (7).]

[$\bar{C}$ (1 pt.) *in 2 pts. ice-cold* HNO_3 (D = 1.48) *stood 24 hrs. gives* (37% *yield* (2)) a prod. of compn. $C_7H_4O_4N_2Cl_2$, white ndls. from dry ether by pptn. with pet. ether, m.p. 109° dec. (2).]

[$\bar{C}$ with boilg. dil. HNO_3 oxidizes (7) to oxalic acid (1:0445); $\bar{C}$ on oxidn. with $K_2Cr_2O_7$ + dil. H_2SO_4 gives (4) 6-chloro-2-methylbenzoquinone-1,4 (6-chloro-*p*-toluquinone) [Beil. VII-650, VII_1-(353)], yel. ndls., vol. with steam, m.p. 90° (4); $\bar{C}$ digested with aqua regia for 1½ hrs. at 100° gives (16% yield (5)) 3,5,6-trichloro-2-methylbenzoquinone-1,4 (trichloro-*p*-toluquinone) [Beil. VII-651, VII_1-(354)], yel. lfts. from alc., m.p. 233° (5); $\bar{C}$ with CrO_3/AcOH gives a mixt. (4) of chlorinated quinones.]

[$\bar{C}$ does not react with PCl_5 (10); $\bar{C}$ on monosulfonation with fumg. H_2SO_4 (65% SO_3) at 50° yields (11) 4,6-dichloro-2-methylphenolsulfonic acid-3; for condensation of $\bar{C}$ with benzaldehydesulfonic acid-4 and use as mothproofing agt. see (12).]

[$\bar{C}$ in MeOH/KOH refluxed 6½ hrs. with MeI (74% yield (3)), or $\bar{C}$ in aq. alk. with Me_2SO_4 (1) gives the *corresp. methyl ether (4,6-dichloro-2-methylanisole)*, m.p. 33° (1), 29–30° (3), b.p. 230° (1); $\bar{C}$ in aq. alk. soln. treated with Et_2SO_4 gives (1) corresp. ethyl ether (4,6-dichloro-2-methylphenetole), m.p. 27.5° (1).]

V. ALPHABETICAL NAME INDEX TO COMPOUNDS OF ORDER 3

1. Note that this index refers only to numbered compounds of Order 3; for practical reasons it cannot include the large number of related products which are incidentally mentioned within the text of these numbered individuals.

2. In this alphabetical name index all literal prefixes (such as those below) are ignored in establishing the alphabetical sequence. Note, however, that "iso" is not recognized as a prefix but is construed as an integral part of the name and therefore indexed under the letter I.

3. Within any given group of related prefixes the following sequences are employed:

d,l- . . . *allo-* . . . *meso-*	h.-m. . . . l.-m.
erythro- . . . *threo-*	*o-* . . . *m-* . . . *p-*
cis- . . . *trans-*	α- . . . β- . . . γ- . . . δ- . . . ω-
prim.- . . . *sec.-* . . . *ter-*	*bis-* . . . *tris-*
sym.- . . . *unsym.-*	solid . . . liquid

4. Note that except when needed to distinguish from other stereoisomers the prefix *d,l* is omitted from the alphabetical index names even when included in text of the individual compound.

5. Whenever in a particular name the syllable (di) is inserted in parentheses to avoid possible ambiguity, such syllable is ignored in establishing the alphabetical sequence.

6. For a given family of derivatives of the same halogen-free parent, the sequence of listing is based upon the parent, e.g., all the dichloro substitution products of naphthol-1 precede all those derived from naphthol-2.

A

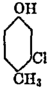
Ⓓ 4,6-Dichloro-2-methylphenyl acetate: m.p. 28.5°, b.p. 254° (1). [From C̄ with excess Ac_2O + a drop of conc. H_2SO_4 htd. 4 hrs. at 100° (1).]

Ⓓ 4,6-Dichloro-2-methylphenyl benzoate: m.p. 114°, b.p. 240° (1). [From C̄ with benzoyl chloride (1).]

3:1020 (1) Bures, *Chem. Listy* **21**, 108–114, 148–162, 221–227, 261–265 (1927); *Cent.* **1927**, II 1344; *C.A.* **22**, 63 (1928). (2) Zincke, *Ann.* **417**, 199, 206–207, 221–222 (1918). (3) Martini, *Gazz. chim. ital.* **29**, II 60–61 (1899). (4) Claus, Schweitzer, *Ber.* **19**, 927–929 (1886). (5) Chulkov, Parini, Barshev, *Org Chem. Ind.* (*U.S.S.R.*) **3**, 410–412 (1937); *Cent.* **1938**, II 305; *C.A.* **31**, 7047 (1937). (6) Huston, Neeley, *J. Am. Chem. Soc.* **57**, 2177 (1935). (7) Claus, Riemann, *Ber.* **16**, 1601–1602 (1883). (8) Tanaka, Morikawa, Sakamoto, *J. Chem. Soc. Japan* **51**, 275–277 (1930), *C.A.* **26**, 706 (1932). (9) Korczynski, *Cent.* **1909**, II 806. (10) Anschutz, *Ann.* **454**, 108 (1927).

(11) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; *Cent.* **1932**, II 2371. (12) Weiler (to I.G.), Ger. 548,822, April 20, 1932; *Cent.* **1932**, II 799.

3:1025 3-CHLORO-4-METHYLPHENOL (3-Chloro-*p*-cresol)



C_7H_7OCl Beil. VI-402, VI_1—, VI_2—

M.P. 55° (1) (2) B.P. 228° at 760 mm. (2)
229° at 735 mm. (1)

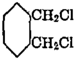
Long colorless ndls., markedly sol. in aq. and volatile with steam (1). — Eas. sol. alc., ether, or C_6H_6.

[For prepn. (77% yield) from 3-chloro-4-methylaniline [Beil. XII-988] via diazo reaction see (1).]

C̄ dislvd. in 20% NaOH and shaken with $(CH_3)_2SO_4$ gives 95% yield of corresponding methyl ether, viz., 3-chloro-4-methylanisole, b.p. 212° (1). [Oxidn. of this ether with dil. aq. $KMnO_4$ yields (1) 2-chloro-4-methoxybenzoic acid [Beil. X-175], ndls. from aq., m.p. 208° (1).]

3:1025 (1) Ullmann, Wagner, *Ann.* **355**, 367–368 (1907). (2) Badische Anilin und Soda-fabrik, Ger. 156,333, Nov. 14, 1904; *Cent.* **1904**, II 1672.

3:1040 *o*-XYLYLENE (DI)CHLORIDE (ω,ω'-Dichloro-*o*-xylene)



$C_8H_8Cl_2$ Beil. V-364, V_1—, V_2-(283)

M.P. 55° (1) (2) B.P. 239–241° (3)
54.6–54.8° (3) 130–135° at 19 mm. (2)
54–55° cor. (5)

Cryst. (from pet. eth.). — Sublimes. — Sol. alc., ether, $CHCl_3$, lgr. Powerful lachrymator.

[For prepn. from *o*-xylyleneglycol + boilg. conc. HCl see (3); from *o*-xylene (1:7430) + PCl_5 at 190° see (3) (4); from *o*-xylene (1:7430) + Cl_2 in sunlight see (1); for formn. of C̄ (13%) during chloromethylation of benzyl chloride (3:8535) see (5).]

C̄ on oxidn. with $KMnO_4$ yields phthalic ac. (1:0820).

3:1040 (1) Radziewanowski, Schramm, *Cent.* **1898**, I 1019. (2) Quelet, *Bull. soc. chim.* (4) **53**, 223 (1934). (3) Colson, *Ann. chim.* (6) **6**, 108–109 (1885). (4) Colson, Gautier, *Ann. chim.* (6) **11**, 22 (1887). (5) Kulka, *Can. J. Research* **23-B**, 107 (1945).

E

F

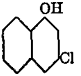
G

H

U

V

X

3:4170 3-CHLORONAPHTHOL-1  $C_{10}H_7OCl$ Beil. VI —
VI₁—
VI₂-(581

M.P. 143° (1)
134–135° (2)

Ndls. from lgr. (2), C_6H_6, alc. or 80% AcOH (1). — Volatile with steam (1).

[For prepn. of C̄ from 3-chloronaphthylamine-1 (1) via diazotization and hydrolys of the diazonium salt with steam see (1); from 2,3,4-trichloronaphthol-1 [Beil. VI-613 by partial reduction with HI ($D = 1.7$) in AcOH on boilg. 7 hrs. (100% yield) see (2)]

C̄ is sol in aq alk., and the result. soln. couples with solns. of diazonium salts (1).

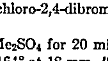
C̄ with Br_2 aq. (and alk.?) gives 3-chloro-2,4-dibromonaphthol-1, pr. from 90% formic acid, m.p. 112° (1).

[C̄ in 10% aq KOH shaken with Me_2SO_4 for 20 min. gives (81% yield (2)) 3-chloronaphthol-1 methyl ether, oil, b.p. 162–164° at 18 mm. (2).]

Ⓓ **3-Chloro-1-naphthyl acetate:** ndls. from lgr., m.p. 69° (2). [From C̄ with acetyl chloride in C_6H_6 on refluxing 3 hrs. in C_6H_6 (66% yield (2)).]

Ⓓ **3-Chloro-1-naphthyl benzoate:** ndls. from lgr., m.p. 118–119° (2). [From C̄ in 10% aq. KOH on shaking with BzCl (71% yield (2)).]

3:4170 (1) Hodgson, Elliott, *J. Chem. Soc.* **1934**, 1707. (2) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 385–387 (1922).

3:4200 2,6-DICHLOROBENZOIC ACID  $C_7H_4O_2Cl_2$ Beil. IX - 343
IX₁-(141)

M.P. 144° (1) (2)
143.7° (3)
143–144° (4)
141.5–142.5° (5)

Many recorded m.p.'s lower than these values [cf. Beil. IX-343 and (3)] were on sampl now known to have been impure.

Cryst. from lgr. (1) or mixt. of C_6H_6 + lgr. (4) (3); pr. from aq., tbls. from C_6H_6, ndl from alc. — Can also be purified by distn. in vac. (1). — Volatile with steam (?).

[For prepn. of C̄ from 2,6-dichlorotoluene (3:6270) (57% yield (4)) via brominat to 2,6-dichlorobenzyl bromide, conversion to corresp. acetate, and oxidn. of latter w $KMnO_4$ see (1) (4); from 2,6-dichlorobenzaldehyde by oxidn. with $KMnO_4$ see (2); (5 older less satisfactory methods see Beil. IX-343.]

C̄ on htg. begins to lose CO_2 at 235° (5). [C̄ htd. with a large excess 50% aq. KOH 150° for 24 hrs. was recovered unchanged to extent of 90% (9).]

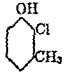
C̄ on nitration under stated conditions (1) gives 94% yield 2,6-dichloro-3-nitrobenzoi acid, cryst. from toluene, m p. 152° (1).

C̄ (as KĀ) htd. with aniline + K_2CO_3 + Cu in amyl alc. gives small yield of diphenyl aminecarboxylic acid-2, cryst. from C_6H_6, m.p. 181° (1). [Note loss of both chlorin atoms.]

C̄ htd. with acetamide for 6 hrs. at 225–235° gave 93% yield (5) *m*-dichlorobenzen (3:5960), b.p. 172°.

C̄ htd. with PCl_5 (6) or with $SOCl_2$ + pyridine (4) yields 2,6-dichlorobenzoyl chloride, b.p. 142–143° at 21 mm. (6), 126–128° at 18 mm. (7).

3:1055 2-CHLORO-3-METHYLPHENOL (2-Chloro-*m*-cresol)



C_7H_7OCl Beil. VI — VI_1— VI_2-(355)

M.P. 55–56° (1) B.P. abt. 194° (1)
49–50° (2)

Transparent cryst. (1) (2) from pet. eth. — Very spar sol cold aq.; pronounced phenolic odor (1).

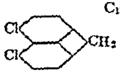
[For prepn. from *m*-cresoldisulfonic acid by chlorination see (2); from 2-nitro-3-methylphenol via 2-amino-3-methylphenol see (2), from 2-chloro-3-methylanisole by boilg. with HI see (1).]

C̄ treated with $(CH_3)_2SO_4$ + aq NaOH gives its methyl ether, 2-chloro-3-methylanisole, pr. from light pet. eth., m.p. 24.2°, b.p. 218 5° (1) [This methyl ether on oxidn. with dil. $KMnO_4$ (7¼ hrs. for 5 g.) gave (1) 2-chloro-3-methoxybenzoic acid, stout colorless rectangles, m.p. 160.5° (1), 160° (3), Neut Eq. 186 5.]

- Ⓓ *2-Chloro-3-methylphenyl benzoate: from C̄ + BzCl + pyridine, pr from alc., m.p.* 55–56° (2). [Note that this value is numerically the same as C̄ and that the deriv. must be distinguished from orig C̄, e.g., by mixed m p or behavior with alk]
- Ⓓ **2-Chloro-3-methylphenyl benzenesulfonate:** from C̄ + benzenesulfonyl chloride + pyridine; pl. from alc., m.p. 58–58 5° (2) [See note for above deriv]
- Ⓓ **2-Chloro-3-methylphenyl *p*-toluenesulfonate:** from C̄ + *p*-toluenesulfonyl chloride + pyridine; pr. from alc. m.p. 96° (2) [Note that this deriv does not distinguish C̄ from 6-chloro-3-methylphenol (3:0700) or 4-chloro-3-methylphenol (3:1535).]

3:1055 (1) Gibson, *J. Chem. Soc.* 1926, 1424–1428 (2) Huston, Chen, *J. Am. Chem. Soc.* 55, 4214–4218 (1933). (3) Hodgson, Beard, *J. Chem. Soc* 1926, 150

3:1057 4,4'-DICHLORODIPHENYL-METHANE (Di-(p-chlorophenyl)methane)



$C_{13}H_{10}Cl_2$ Beil. V - 590 V_1— V_2-(501)

M.P. 55–56°	**(1)**	**B.P. 337°** at 760.5 mm.	(5)
55°	(2) (3) (4) (5)	**186–190°** at 18 mm.	(1)
54–55°	(7)	**208–210°** at 15 mm.	(3)

Colorless ndls. from MeOH.

[For prepn. of C̄ from 4,4'-dichlorobenzophenone (3.1270) by reduction with conc. HI + red P in boilg. AcOH (4) or as by-prod of reduction with Zn dust + AcOH + dil. H_2SO_4 (5) see indic. refs ; from 4,4'-diaminodiphenylmethane [Beil XII-238, XII_1-(71)] by tetrazotization and subsequent use of Cu_2Cl_2 reaction (50% yield) see (1)]

[For prepn. of C̄ from chlorobenzene (3 7903) by action of *sym* -dichloro-dimethyl ether (3:5245) in pres. of $ZnCl_2$ (3) or better (alm 100% yield (3)) conc H_2SO_4 at 40°, or by action *in pres. of H_2SO_4 of various other formaldehyde derivs. (6), see indic. refs.; from* p-chlorobenzyl chloride (3:0220) with chlorobenzene (3 7903) + conc. H_2SO_4 (67% yield (3)) see indic. refs.]

[For prepn of C̄ from "DDT" (3 3208), from 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethylene (3:2138), or from di-(p-chlorophenyl)acetic acid (3:4612) by action of KOH in ethylene glycol refluxed 8–10 hrs. (alm. 100% yield) see (2)]

[For formn. of C̄ (21% yield) from hydrazone of 4,4′-dichlorobenzophenone (3:4270) via Wolff-Kishner reduction see (7).]

C̄ on oxidn. with CrO_3/AcOH readily gives (3) 4,4′-dichlorobenzophenone (3:4270), m.p. 145° (3).

C̄ on dinitration by addn. to 8 pts. fumg. HNO_3 (D = 1.5) with water cooling gives (1) *3,3′-dinitro-4,4′-dichlorophenylmethane*, white pl. from AcOH, m.p. 198–199° (1), 196° (3); this prod. with piperidine splits out 2 moles HCl giving (1) 3,3′-dinitro-4,4′-dipiperidinodiphenylmethane, m.p. 183–184° (1). — [Note, however, that C̄ dislvd. in 9–10 wt. pts. conc. HNO_3 (D = 1.42) and kept at 100° for 1 hr. (3) gives some of the above dinitro derivative but is also in part oxidized and nitrated (or vice versa) with formn. of 3,3′-dinitro-4,4′-dichlorobenzophenone, ndls. from alc., m.p. 132° (3); see also text of 4,4′-dichlorobenzophenone regarding nitration.]

3:1057 (1) LeFevre, Turner, *J. Chem. Soc.* **1927**, 1120. (2) White, Sweeney, *U.S. Pub. Health Repts.* **60**, 66–71 (1945). (3) Stephen, Short, Gladding, *J. Chem. Soc.* **117**, 522–523 (1920). (4) [illegible] (5) [illegible] 25, 412 (1906).
(6)
405(

3:1058 β,β-DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ Beil. II-252

$Cl_2CH.CH_2.COOH$ II₁— II₂—

M.P. 56° (1)

Colorless cryst., eas. sol. aq., alc., ether, C_6H_6, or $CHCl_3$.

[For prepn. of C̄ from β-chloroacrylic acid (3:2240) by addn. of 1 HCl with 40% aq. HCl in s.t. at 80–85° for 35–40 hrs. (yield not stated) see (1).]

C̄ with alc. KOH splits out 1 HCl giving (1) β-chloroacrylic acid (3:2240).

C̄ with $SOCl_2$ at 75–80° for 3–4 hrs. gives (2) β,β-dichloropropionyl chloride (3:9032-A).

—— **Methyl β,β-dichloropropionate**: unreported.

—— **Ethyl β,β-dichloropropionate**: b.p. 171–175° (1). [From C̄ in EtOH with dry HCl (1).]

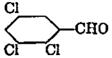
Ⓓ **β,β-Dichloropropionamide**: ndls. from $CHCl_3$, m.p. 140° (1). [From ethyl β,β-dichloropropionate (above) with conc. aq. NH_4OH on shaking at room temp. (1).]

—— **β,β-Dichloropropionanilide**: unreported.

—— **β,β-Dichloropropion-*p*-toluidide**: unreported.

3:1058 (1) Otto, *Ann.* **239**, 266–272 (1887). (2) Leimu, *Ber.* **70**, 1050 (1937).

3:1060 2,3,5-TRICHLOROBENZALDEHYDE $C_7H_3OCl_3$ Beil. S.N. 635



M.P. 56° (1)

Colorless ndls. (from dil. alc.) with characteristic pungent odor. — Volatile with steam. — [Note that a patent abstract gives m.p. as 75–76° (2).]

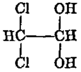
[For prepn. of C̄ from 3-amino-2,5-dichlorobenzaldehyde (presumably by diazotization and use of Cu_2Cl_2 reaction) see (1).]

C̄ on oxidn. with neutral $KMnO_4$ gives (1) 2,3,5-trichlorobenzoic acid (3:4485), m.p. 162–163°.

C̄ with PCl_5 should give 2,3,5-trichlorobenzal (di)chloride, but this compd. is unreported in the literature.

—— **2,3,5-Trichlorobenzaldoxime:** unreported.
—— **2,3,5-Trichlorobenzaldehyde phenylhydrazone:** unreported.
—— **2,3,5-Trichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.
—— **2,3,5-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unreported.

3:1060 (1) Hodgson, Beard, *J. Chem. Soc.* **1927**, 2381–2382. (2) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; *Cent.* **1926**, II 2355; [*C.A.* **21**, 1361 (1927)], French 603,-650, April 20, 1926; *Cent.* **1926**, II 2355; not in *C.A.*

3:1085 DICHLOROACETALDEHYDE HYDRATE  $C_2H_4O_2Cl_2$ Beil. I-614 I_1— I_2—

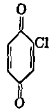
M.P. 56–57° (1) (4) **B.P.** 118–121° (1)
55–56° (2) 96–97.5° (2)

Cryst. from C_6H_6 (3). — Eas. sol. aq or ether; sol. CS_2.

[For prepn. of C̄ from dichloroacetaldehyde (3:5180) with a limited amt. of cold aq. see (2); for formn. of C̄ from α,β,β-trichloroethyl ethyl ether with aq. see (2); for formn. of C̄ as by-product of actn. of Cl_2 on paraldehyde in prepn. of butyrchloral (3:5910) see (2); for formn. of C̄ from chloral hydrate with Al/Hg + aq. see (5).]

C̄ with conc. H_2SO_4 yields (3) dichloroacetaldehyde (3:5180), b.p 89°.

3:1085 (1) Denaro, *Gazz. chim. ital.* **14**, 119–120 (1884). (2) Oddo, Mameli, *Gazz chim. ital.* **33**, II 398–399 (1903). (3) Friedrich, *Ann* **206**, 251–254 (1880). (4) Ingold, *J. Chem. Soc.* **125**, 1537 (1924). (5) Deodhar, *J. Indian Chem. Soc.* **11**, 84 (1934).

3:1100 2-CHLOROBENZOQUINONE-1,4 (Chloroquinone)  $C_6H_3O_2Cl$ Beil. VII-630 VII_1-(346)

M.P. 57° (1) (2) (3) (4) (5) (6) (7) (14) (15)
56.0–56.5° cor. (8)
56° (9)
55–57° (10)
54° (11)

[See *also 2-chlorohydroquinone* (3:3130).]

Pale yel. cryst.; eas. sol. aq., alc., ether, $CHCl_3$. — Volatile even at ord. tem. — Gradually dec. by light (3) (for study of photochem decompn. in alc. see (12)). — Sol. in conc. H_2SO_4 on warming with brown black color.

[For prepn. of C̄ from 2-chlorohydroquinone (3:3130) by oxidn. with $NaClO_3$ + H_2SO_4 + V_2O_5 in AcOH (92% yield (13)), with $K_2Cr_2O_7$ + H_2SO_4 (yield: 89% (14), 84% (1)) (7), with MnO_2 + dil. H_2SO_4 (56% yield (1)), or with PbO_2 in C_6H_6 (2) see indic. refs: from 2-chloro-4-aminophenol [Beil. XIII-510, $XIII_1$-(181)] by oxidn. with $K_2Cr_2O_7$ +

H_2SO_4 (68% yield (8)) (10) (15) see indic. refs.; from benzoquinone-1,4 (1:9025) in CCl_4 with ⅓ mole HCl gas see (9); for formn. of C̄ (together with other prods.) from oxidn. of copper salt of quinic acid [Beil. X-535, X_1-(270)] with MnO_2, NaCl + dil. H_2SO_4 see (16)]

[For use of C̄ as vulcanization accelerator see (17); for use as seed disinfectant see (18); for study of bactericidal action see (19).]

C̄ on reductn. with aq. SO_2 gives *(16) (7) 2-chlorohydroquinone (3:3130)* (note, however, that C̄ in dil. aq. NaOH under N_2 with SO_2 is in part reduced to 2-chlorohydroquinone and in part sulfonated (20)). [For studies on oxidn.-reductn. potential of system C̄ + 2-chlorohydroquinone (3:3130) see (1) (2) (3) (21) (22) (23) (24).] — [C̄ with 2-chlorohydroquinone (3:3130) yields (1) (16) (25) the corresp. quinhydrone, monohydrate, violet pr. with green shimmer, m.p. 70–72° (25), anhydrous form, m.p. 93–94° (25), 67° (1); C̄ with hydroquinone (1:1590) gives (25) (6) corresp. quinhydrone, dark green ndls. from alc., m.p. 132–133° (25), 130–135° (6).]

[C̄ in $CHCl_3$ with HCl gas (7) (26) or C̄ with hot conc. HCl (83% yield (10)) gives only 2,5-dichlorohydroquinone (3:4690), but C̄ in ether with HCl gas (26) or C̄ dislvd. in cold dil. HCl ($D = 1.10$) (26) gives both 2,3-dichlorohydroquinone (3:4220) and 2,5-dichlorohydroquinone (3:4690); C̄ refluxed with conc. HBr gives (27) 2-chloro-5-bromohydroquinone [Beil. VI-853], ndls m.p. 171–172° (28) (diacetate, m.p. 145–146° (28)); C̄ in alc. with KCN + H_2SO_4 *gives in good yield (29) 3,6-dihydroxyphthalonitrile (2,3-dicyanohydroquinone)* [Beil. X-551]]

[C̄ with Ac_2O + trace H_2SO_4 yields (29) a chloro-hydroxyhydroquinone triacetate, ndls. from alc., m.p. 96–97° (29); C̄ with AcCl gives (28) 2,5-dichlorohydroquinone diacetate, m.p. 141°; C̄ with AcBr gives (28) 2-chloro-5-bromohydroquinone diacetate, m.p. 145–146° (28)]

[C̄ with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which upon oxidn. yields (30) 2-chloro-6,7-dimethylnaphthoquinone-1,4; for reactn. of C̄ with diazotized aniline see (31); for addn. prods. of C̄ with hexamethylbenzene (1:7265) see (5).]

[C̄ in alc. or AcOH on warming with aniline gives (32) 2,5-dianilinobenzoquinone-1,4 [Beil. XIV-138, $XIII_1$-(413)], red-br. scales, m.p. 345° u.c.]

[C̄ in dil. alc. with $NH_2OH.HCl$ as directed (33) gives 2-chlorobenzoquinone-1,4-monoxime-4 (purified (with difficulty) by conv. to the mixt. of stereoisomeric oxime acetates followed by hydrolysis), m.p. 142° (34), 148° dec. (35); this prod. by special treatment yields a dioxime [Beil. VII-632].]

C̄ in cold dil. alc with semicarbazide HCl gives (36) 2-chlorobenzoquinone-1,4-semicarbazone-4, deep yel. cryst. from acetone + pet. ether, m.p. 185° dec. (36); this prod. on boilg. with dil. aq. NaOH yields *o*-chlorophenol (3:5980) + N_2 + CO_2 + NH_3 (36); C̄ does not give a *bis*-semicarbazone (36).

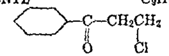
3:1100 (1) Conant, Fieser, *J. Am Chem. Soc.* **45**, 2201–2202 (1923). (2) Hunter, Northley, *J. Phys. Chem.* **37**, 885–886 (1933). (3) LaMer, Baker, *J. Am. Chem. Soc.* **44**, 1956, 1960 (1922). (4) Clarke, *J. Ind Eng. Chem.* **10**, 891–895 (1918). (5) Pfeiffer, *Ann.* **412**, 291–292 (1916). (6) Siegmund, *J. prakt. Chem.* (2) **92**, 360–361 (1915). (7) Levy, Schultz, *Ann.* **210**, 145–147 (1881). (8) van Erp, *Ber.* **58**, 663–665 (1925). (9) Michael, Cobb, *J. prakt. Chem.* (2) **82**, 304–305 (1910). (10) Eckert, [illegible]

(11) Kehrmann, *Ber.* **21** [illegible] *Chem. Soc.* **52**, 3557–3562 (1930). (13) Underv[illegible] 1936). (14) Den Hollander, *Rec. trav. chim.* **39**, [illegible] (1886). (16) Städeler, *Ann.* **69**, 302–309 (1849). (17) Fisher [illegible] *Cent.* **1933**, I 3133. (18) I.G., Brit. [illegible] Austrian 108,914, Feb. 25, 1928; *Cent.* [illegible] 43-T, 352–354 (1924). (20) Dodgson, *J. Chem. Soc.* **1930**, 2498–2502.

(21) Hunter, Kvalnes, *J. Am. Chem. Soc.* **54**, 2874–2875, 2878 (1932). (22) Kvalnes, *J. Am. Chem. Soc.* **56**, 668 (1934). (23) Conant, Fieser, *J. Am. Chem. Soc.* **44**, 2484–2485, 2489 (1922).

(24) Conant, *J. Am. Chem. Soc.* **49**, 293–297 (1927). (25) Ling, Baker, *J. Chem. Soc* **63**, 1318–1319 (1893). (26) Peratoner, Genco, *Gazz. chim. ital* **24**, II 394 (1894). (27) Ref. 7, pp. 160–161. (28) Schulz, *Ber.* **15**, 656 (1882). (29) Thiele, Günther, *Ann.* **349**, 48, 52 (1906) (30) I.G., Brit. 324,661, Feb. 27, 1930; French 677,296, March 6, 1930, 677,781, March 14, 1930; *Cent.* **1930**, II 810
Cent. **1931**, I 1676, cf Günther (to General
Ar t **1930**, II 137. (32) Niemeyer, *Ann.* **228**,
33), *Ber* **21**, 3316–3317 (1888) (34) Bridge, *Ann.* **277**, 100–101 (1893). (35) Fischer, Neber, *Ber* **45**, 1097 (1912) (36) Heilbron, Henderson, *J. Chem. Soc.* **103**, 1416 (1913).

3:1115 β-CHLOROETHYL PHENYL KETONE C_9H_9OCl **Beil. VII - 302**
(β-Chloropropiophenone) **VII₁-(161)**



M.P. 57–58° (1)
57° (2)
55–56° (3)

49–50° (4) (5)
49° (3)

See text.

Lfts. from pet. ether (5), alc. (1) (5), or ether (2), eas. sol. in org. solv. except lgr. — C̄ on distn. even under reduced press. loses HCl with partial conversion (2) to phenyl vinyl ketone; nevertheless in small amts. of less than 10 g C̄ may be distd below 2 mm (3); in general, however, unnecessary htg of C̄ should be avoided (4).

[For prepn. of C̄ from β-chloropropionyl chloride (3 5690) with C_6H_6 + $AlCl_3$ (yield: 90% (1), 80–90% (6), 65% (5)) see indic. refs. (note, however, that this method is best suited for small runs (6) since with large units much ω-benzylacetophenone [Beil. VII-444, VII_1-(237)], m p. 72°, is also formed (6) (4); furthermore that C̄ prepd by this method melts at 49° even when white, unless it is treated with decolorizing carbon (3), for prepn. from benzoyl chloride (3:6240) + ethylene + $AlCl_3$ (87–92% yield) in special apparatus see (3); for prepn. of C̄ from phenyl vinyl ketone + HCl gas in dry ether see (2); for formn. of C̄ from ethyl phenyl ketone (propiophenone) (1·5525) + Cl_2 see (7)]

[C̄ htd 15–30 min. in AcOH with 1½ moles NaOAc or KOAc, then poured into aq. and neutralized with K_2CO_3, gives (8) β-acetoxypropiophenone, lfts from MeOH, m.p. 53–54° (8); C̄ in hot alc. treated with KOAc, then with aq. NaCN, gives (65% yield (9)) β-cyanopropiophenone, lfts. from alc., m.p. 76° (2,4-dinitrophenylhydrazone, m p. 141°; corresp. β-benzoylpropionic acid, m.p. 116° (9))]

[C̄ under certain circumstances reacts as potential phenyl vinyl ketone: e.g., C̄ + KOAc in hot MeOH treated with phenyl-nitromethane + NaOMe gives (82% yield (10)) (presumably t
C_6H_6 + p
with desox
1,5, m p. 95° (monoxime, m.p. 131°; dioxime, m p. 162°; 2,4-dinitrophenylhydrazone, m p. 221°) (6)]

C̄ in AcOH reduced with H_2 + Adams cat gives (11) 3-chloro-1-phenylpropanol-1, b p 130–132° at 8 mm. (p-nitrobenzoate, m.p. 62–63°) (11).

[For study of rate of reactn. of C̄ with KI in acetone see (5), for study of C̄ with Na + liq NH_3 see (12); for behavior of C̄ with anthrone see (13) (14) (15); for reactn of C̄ with C_6H_5MgBr yielding ω-benzylacetophenone (β-phenylpropiophenone) (cf. above) see

(16) (2); for reactn. of C̄ with sodium benzenesulfinate giving (68% yield) β-(benzenesulfonyl)propiophenone, m.p. 98° see (17).]

C̄ htd. with aq. + aniline for 30 min. at 100° gives (4) β-anilinopropiophenone, pl. from alc., m.p. 111–112° (4); note, however, that C̄ htd. with aniline + aniline HCl yields (4) 4-phenylquinoline.

[C̄ in MeOH boiled 3 hrs. with hydrazine hydrate (87%) gives (28% yield (18)) 3-phenylpyrazoline-2, b.p. 164° at 17 mm., m.p. 44–45° (18) (1-nitroso deriv., m.p. 152.5–153.5°; *1-carbomethoxy deriv., m.p. 123–124°; 1-carbethoxy deriv., m.p. 72°) (18).* — C̄ (or phenyl vinyl ketone) with phenylhydrazine yields by ring closure (19) 1,3-diphenylpyrazoline-2 [Beil. XXIII-153], m.p. 152–153° (19).]

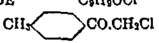
[C̄ htd. in alc. with $NH_2OH.HCl$ + NaOH gives very small yield (8) corresp. oxime, m.p. 56–58°; from the mother liquor, however, is obtd. (8) as a result of ring closure 3-phenylisoxazoline, tbls. from lgr. m.p. 66–67°, which is the sole product starting from β-acetoxypropiophenone (above); another by-product of oximation is *N,N-bis*-(β-benzoylethyl)hydroxylamine dioxime, m.p. 154–155° (8).]

- Ⓓ **β-(Phthalimido)propiophenone:** cryst. from alc., m.p. 130° (1). [From C̄ + K phthalimide in 68% yield on htg. in s.t. for 1 hr. at 130–140° (1); on hydrolysis with fumg. HCl in AcOH in s.t. at 145–150° for 1 hr. this prod. gives 95% yield (1) β-aminopropiophenone hydrochloride, cryst. from abs. alc., m.p. 128° (1).]
- Ⓓ **1-Methyl-3-carbohydrazidopyridinium *p*-toluenesulfonate:** cryst. from alc., m.p. 171° cor. (20). [From *C̄ +* nicotinic *hydrazide/methyl p-toluenesulfonate addn.* prod. as directed (20).]

3:1115 (1) Hale, Britton, *J. Am. Chem. Soc.* **41**, 845–847 (1919). (2) Kohler, *Am. Chem. J.* **42**, 389 (1909). (3) Allen, Cressmann, Bell, *Can. J. Research* 8, 440–446 (1933). (4) Kenner, Statham, *J. Chem. Soc.* **1935**, 301. (5) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 239–240, 251 (1924). (6) Allen, Barker, *J. Am. Chem. Soc.* **54**, 740–742 (1932). (7) Szper, *Bull. soc. chim.* (4) **51**, 656 (1932). (8) von Auwers, Müller, *J. prakt. Chem.* (2) **137**, 124–127 (1937). (9) Allen, Gilbert, Young, *J. Org. Chem.* **2**, 231 (1937). (10) Allen, Bridgess, *J. Am. Chem. Soc.* **51**, 2153–2154 (1929).
(11) [illegible] 2, 2826
(1930). [illegible] anishi,
Proc. I[illegible] (15)
Kränzl[illegible] (16)
Weizmann, Bergmann, *J. Chem. Soc.* **1936**, 402. (17) Kohler, Larsen, *J. Am. Chem. Soc.* **57**, 1449 (1935). (18) von Auwers, Heimke, *Ann.* **458**, 207–208 (1927). (19) von Auwers, *Ber.* **65**, 832–833 (1932). (20) Allen, Gates, *J. Org. Chem.* **6**, 596–601 (1941).

3:1130 *p*-METHYLPHENACYL CHLORIDE C_9H_9OCl Beil. VII - 309

(Chloromethyl *p*-tolyl ketone, ω-chloro-*p*-methylacetophenone) VII₁-(165)



M.P.	57–58° (1) (5)	B.P.	260–263°	(2)
	55.5–56° (2) (3)		260–265° sl. dec.	(3)
	54.5–55° (4)		113° at 4 mm.	(4)

Ndls. from alc.; eas. sol. alc., ether.

[For prepn. from toluene (1:7405) + chloroacetyl chloride (3:5235) + $AlCl_3$ see (2) (3); from toluene + chloroacetic acid anhydride (3:0730) + $AlCl_3$ (46–59% yield) see (4).]

C̄ on oxidn. with alk. $KMnO_4$ gives terephthalic ac. (1:0910) (2).

C̄ with NaI in acetone gives *p*-methylphenacyl iodide, ndls. from alc., m.p. 42–43° (11).

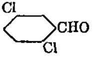
C̄ refluxed with alc. KOAc yields (2) *p*-methylphenacyl acetate [Beil. VIII-113], ndls from alc., m.p. 83–83.5° (2), 85–86° (1).

C̄ dislvd. in alc. warmed at 60° with $Na_2S.9H_2O$ dislvd. in aq. gives (5) (73% yield (6)) *bis*-(*p*-methylphenacyl)sulfide, pale yel. ndls. from alc., m.p. 88° (5); 88.8–89.3° (6). [For detn. of C̄ by titration of residual chloride ion from this reaction see (5).]

[For reactions of C̄ with phenol + KOH + Cu see (7); with phenyl-*p*-bromophenyl-, *p*-nitrophenyl-, *o*-tolyl-, and *p*-tolyl-hydrazines see (5); with Br_2 see (8); with KCN or KSCN see (9); with alc. NaOEt see (10).]

3:1130 (1) von Auwers, *Ber.* **39**, 3761 (1906). (2) Collet, *Bull. soc. chim.* (3) **17**, 507–508 (1897). (3) [illegible] *Am. Chem. Soc.* **46**, 1893–1894 (1924). [illegible] Chrzaszc-Zewska, Chwalinski, *Roczniki* [illegible] (1929). (7) Sabetay, *Bull. soc. chim.* [illegible] *Chem.* **10**, 541–544 (1930), *Cent.* **1930**, II 3273. (9) Rabcewicz-Zubkowski, Kaflinska, *Roczniki Chem.* **10**, 555–569 (1930); *Cent.* **1930**, II 3274. (10) Almström, *Ber.* **47**, 848–849 (1914).
(11) Jacobs, Heidelberger, *J. Biol. Chem.* **21**, 456 (1915).

3:1145 2,5-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII -237 VII₁—



M.P. 58° (1)	**B.P. 231–233° (1)**
57–58° (2) (4)	**230–233° (2)**
57° (3)	

Ndls. from alc. (4). — Very eas. sol. alc., ether, $CHCl_3$, C_6H_6, CS_2, AcOH (4). — Eas. volatile with steam (4). — Sol. in conc. H_2SO_4 with olive-yel. color; repptd. in cryst. form on dilution (4) (8).

[For prepn. of C̄ from benzaldehyde (1:0195) by chlorination in presence of $SbCl_5$ + I_2 see (5) (1) (9); from 2,5-dichlorotoluene (3:6245) by chlorination to 2,5-dichlorobenzal (di)chloride (3:0490) (m.p. 42°) and hydrolysis of the latter with $CaCO_3$ + H_2O see (1); from 5-nitro-2-chlorobenzaldehyde via reduction to 5-amino-2-chlorobenzaldehyde followed by diazotization + use of CuCl see (6).]

C̄ with satd. aq. $NaHSO_3$ soln. yields a cpd., C̄.$NaHSO_3$ (5), ndls. fairly eas. sol. aq. but dissociating on warming into C̄ + aq. (5).

C̄ on oxidn. with $KMnO_4$ (2) (4) yields 2,5-dichlorobenzoic ac (3:4340), m p. 152° (2), 152–153° (4). — C̄ with 50% aq. KOH (5) (1) (6) undergoes Cannizzaro reactn. giving (90% yield (6)) 2,5-dichlorobenzyl alc., cryst. from C_6H_6, m.p. 80° (1) (6), and (84% yield (7)) 2,5-dichlorobenzoic ac. (3:4340), cryst. from aq , m.p. 155° (5) (7). — C̄ on reductn. with 4% Na/Hg in alc. yields (1) 2,5-dichlorobenzyl alc., m p. 80° (1).

C̄ with PCl_5 (3) gives (78% yield (3)) 2,5-dichlorobenzal (di)chloride (3:0490), b.p. 118–120° at 14 mm , m p. 42° (8), 43° (3).

C̄ on mononitration as specified (5) gives (100% yield (9)) a mixt. of two isomers; by recrystallization from MeOH (9) or EtOH (5) this mixt. gives (62% yield (9)) 2,5-dichloro-6-nitrobenzaldehyde, lfts. or ndls., m.p. 137° (5); the other more soluble isomer is 2,5-dichloro-3-nitrobenzaldehyde (10), m.p. 66 5–67° (5). [The latter yields a phenylhydrazone, or. ndls , m p. 171°, a *p*-nitrophenylhydrazone, deep or. ndls , m p. 290–292° dec., and on oxidn. with alk. $KMnO_4$ yields 2,5-dichloro-3-nitrobenzoic ac., colorless ndls. from AcOH, m p 220° (10)]

[For conversion of C̄ to 2,5-dichlorostyrene (12) (13) via reaction with MeMgX giving (83% yield (12)) 2,5-dichlorophenyl-methyl-carbinol and dehydration of latter with $KHSO_4$ (37% yield (12)) see indic. refs.]

Binary Systems Contg. $\bar{C}$

Azeotropic Systems

[$\bar{C}$ with pentachloroethane (3:5880) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 3.5 wt. % $\bar{C}$ (25); $\bar{C}$ with *p*-dichlorobenzene (3:0980) forms a const.-boilg. mixt., b.p. 174.0° at 760 mm., contg. about 12 wt. % $\bar{C}$ (26); C with *o*-bromotoluene forms a const.-boilg. mixt., b.p. 180.0° at 760 mm., contg. about 18 wt. % $\bar{C}$ (26).]

Other Physical Data on Binary Systems Contg. $\bar{C}$

$\bar{C}$ + aq. [$\bar{C}$ is eas. sol. aq.; for study of hydration at −35° see (70) cf. (34); for f.p./compn. data see (3); for data on D^{20}_{20} (31) and D^{25}_{25} (71) of aq. solns. see indic. refs.; for n^{18}_{D} (8), n^{20}_{D} (31) cf. (73) see indic. refs.]

$\bar{C}$ + H_2SO_4. [For f.p./compn. data and diagram (no compd. formed) see (10).]

$\bar{C}$ + H_3PO_3. [For f.p./compn. data and diagram (no compd. formed) see (12).]

$\bar{C}$ + AcOH (1:1010). [For f.p./compn. data (no cpd.) (74), D^{25}_{4} (2), viscosity (2), and conductivity (1) see indic. refs.]

$\bar{C}$ + chloroacetic acid (3:1370). [For f.p./compn. data (74), eutectic, m.p. 17.5°, contg. 51.5 mole % $\bar{C}$ (75), see indic. refs.]

$\bar{C}$ + dichloroacetic acid (3:6208). [For f.p./compn. data (74), eutectic, m.p. −11.0°, contg. 36 mole % $\bar{C}$ (75), see indic. refs.]

$\bar{C}$ + miscellaneous cpds. of Order 1. [For f.p./compn. data on following systems see indic. refs.]

$\bar{C}$ with hydrocarbons: $\bar{C}$ + C_6H_6 (1:7400) (5); *$\bar{C}$ + camphene* (76).

$\bar{C}$ with alcohols: $\bar{C}$ + EtOH (1:6130) (14); *$\bar{C}$ + ter-BuOH* (1:6140) (14); *$\bar{C}$ + cetyl alc.* (1:5945) (14); *$\bar{C}$ + d-borneol* (1:5990) (14); *C + l-menthol* (1:5940) (14); *$\bar{C}$ + pinacol* (1:5805) (14); *$\bar{C}$ + meso-erythritol* (1:5825) (6); *$\bar{C}$ + d-mannitol* (1:5830) (14).

$\bar{C}$ with phenols: $\bar{C}$ + phenol (1:1420) (14) (11); *$\bar{C}$ + o-cresol* (1:1400) (11); *$\bar{C}$ + m-cresol* (1:1730) (11); *$\bar{C}$ + p-cresol* (1:1410) (11); *$\bar{C}$ + guaiacol* (1:1405) (14); *$\bar{C}$ + thymol* (1:1430) (11); *$\bar{C}$ + α-naphthol* (1:1500) (11); *$\bar{C}$ + β-naphthol* (1:1540) (11); *$\bar{C}$ + hydroquinone* (1:1590) (14).

$\bar{C}$ with aldehydes: $\bar{C}$ + benzaldehyde (1:0195) (7); *$\bar{C}$ + salicylaldehyde* (1:0205) (7); *$\bar{C}$ + m-hydroxybenzaldehyde* (1:0055) (7); *$\bar{C}$ + p-hydroxybenzaldehyde* (1:0060) (7); *$\bar{C}$ + p-anisaldehyde* (1:0240) (7); *$\bar{C}$ + vanillin* (1:0050) (7); *$\bar{C}$ + piperonal* (1:0010) (7).

$\bar{C}$ with ketones: $\bar{C}$ + acetophenone (1:5515) (7); *$\bar{C}$ + benzophenone* (1:5150) (7); *$\bar{C}$ + p-methoxybenzophenone* (1:5170) (7); *$\bar{C}$ + benzil* (1:9015) (7); *$\bar{C}$ + dibenzalacetone* (1:9024) (7); *$\bar{C}$ + benzoquinone-1,4* (1:9025) (7).

$\bar{C}$ with acids: $\bar{C}$ + acetic acid (1:1010) (74); *$\bar{C}$ + benzoic acid* (1:0715) (74); *$\bar{C}$ + o-toluic acid* (1:0690) (74); *$\bar{C}$ + m-toluic acid* (1:0705) (74); *$\bar{C}$ + p-toluic acid* (1:0795) (74); *$\bar{C}$ + phenylacetic acid* (1:0665) (74); *$\bar{C}$ + cinnamic acid* (1:0735) (74); *$\bar{C}$ + crotonic acid* (1:0425) (74).

$\bar{C}$ with esters: $\bar{C}$ + EtOAc (1:3015) (5); *$\bar{C}$ + α-naphthyl acetate* (1:2124) (5); *$\bar{C}$ + β-naphthyl acetate* (1:2273) (5); *$\bar{C}$ + methyl benzoate* (1:3586) (5); *$\bar{C}$ + ethyl benzoate* (1:3721) (5); *$\bar{C}$ + benzyl benzoate* (1:4422) (5); *$\bar{C}$ + phenyl benzoate* (1:2257) (5); *$\bar{C}$ + methyl cinnamate* (1:2090) (5); *$\bar{C}$ + phenyl salicylate ("Salol")* (1:1415) (5); various others (5).

$\bar{C}$ with ethers: $\bar{C}$ + diethyl ether (1:6110) (77); *$\bar{C}$ + veratrole* (1:7560) (14).

$\bar{C}$ + compounds of Order 2. *$\bar{C}$ + o-nitrophenol* (11); *$\bar{C}$ + m-nitrophenol* (11); *$\bar{C}$ + p-nitrophenol* (11); *$\bar{C}$ + o-nitrobenzaldehyde* (7); *$\bar{C}$ + m-nitrobenzaldehyde* (7); *$\bar{C}$ + p-nitrobenzaldehyde* (7); *$\bar{C}$ + nitropiperonal* (7); *$\bar{C}$ + azobenzene* (78); *$\bar{C}$ + ethyl carbamate (urethane)* (16); *$\bar{C}$ + urea* (78A).

BIOCHEMICAL ASPECTS OF $\bar{C}$

[For study of toxicity of $\bar{C}$ see (79); for study of bactericidal effect see (80) (81).]

PREPARATION OF $\bar{C}$

From chloral (anhydrous). [For prepn. of $\bar{C}$ from chloral (3:5210) by oxidn. with fumg. HNO_3 (82) (83) (84), with HNO_2 (85), with NO_2 at 40–60° (70% yield (86)), or with aq. chlorates + cat. see (312); for formn. of $\bar{C}$ from chloral as by prod. of oxidn. with O_2 see (23).]

From chloral hydrate. [For prepn. of $\bar{C}$ from chloral hydrate (3:1270) by oxidn. with fumg. HNO_3 (63% yield (82)) (85), with $KMnO_4$ (88), with $KClO_3$ (89), with $Ca(OCl)_2$ (15), or with aq. chlorates + cat. (312) see indic. refs.]

From acetic acid. [For formn. (first discovery) of $\bar{C}$ from acetic acid (1:1010) by chlorination with Cl_2 in sunlight see (90).]

From tetrachloroethylene. [For formn. of $\bar{C}$ from tetrachloroethylene (3:5460) by stdg. in aq. in light for 4 months see (91) cf. (92); for many other methods see text of tetrachloroethylene (3:5460) under oxidation.]

From miscellaneous sources. [For formn. of $\bar{C}$ from pentachloroethyl chloroformate [Beil. III-13, III_1-(6)] with aq. on htg. (93), but yield is small (94) owing to other modes of reaction (94); from pentachloroethyl trichloroacetate [Beil. II-210] with aq. (95); from trichloroacetyl chloride (3:5420) (96) or from trichloroacetic acid anhydride (3:6575) (97) (98) with aq.; from β,β,β-trichloroethyl alcohol (3:5775) by oxidn. with fumg. HNO_3 (210), see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$

(See also below under decarboxylation.) Pure $\bar{C}$ shows no tendency to decompose at its b.p. (99). — [However, $\bar{C}$ in presence of pumice begins to decompose about 180° giving (99) HCl, $COCl_2$ (3:5000), CO + CO_2. — $\bar{C}$ in presence of ThO_2 begins to decompose at 160–165° giving (99) the same products, although $\bar{C}$ in presence of ThO_2 above 210° (100) or in presence of kaolin above 230° (100) gives $CHCl_3$ (3:5050), tetrachloroethylene (3:5460), hexachloroethane (3:4835), HCl, CO + CO_2. — $\bar{C}$ in presence of animal charcoal at 135° gives (99) $CHCl_3$ (3:5050) + CO_2, but at 200–300° these are accompanied (100) by a little tetrachloroethylene (3:5460), hexachloroethane (3:4835), HCl, and CO. — $\bar{C}$ at 300° in s.t. for 4 hrs. gives (101) trichloroacetyl chloride (3:5420), CO, CO_2 + HCl.

Reduction of $\bar{C}$

[$\bar{C}$ on partial reduction with Zn + aq. (102), with Cu pwdr. in aq. (103), with Cu pwdr. in C_6H_6 + aniline (104) cf. (105), or $\bar{C}$ on electrolytic reduction (106) gives (yields: 80% (103) (106), 75–85% (104)) dichloroacetic acid (3:6208).]

[$\bar{C}$ on complete reduction with HI at 100° (87), or in aq. soln. with K/Hg (107) (84), or by electrolytic reduction with Pt, Cu, or Pb electrodes (108) gives acetic acid (1:1010).]

[$\bar{C}$ in aq. alc. KOH with H_2/Pd gives up all its chlorine as HCl (109) presumably yielding AcOH (1:1010).]

Reactions Involving the —COOH Group of $\bar{C}$

Decarboxylation of $\bar{C}$

$\bar{C}$ in aq., in aq. alkalies, or in aniline or other organic bases undergoes cleavage into $CHCl_3$ (3:5050) + CO_2; for this decompn. presence of the trichloroacetate ion appears

necessary since in relatively nonbasic solvents it does not occur [e.g., C̄ does not decompose at 25° in C_6H_6 (110), toluene (111), $CHCl_3$ (110) (111), CCl_4 (110), CS_2 (110), isoamyl alc. (117), acetone (110), ether (110), ethyl acetate (117), ethyl benzoate (110), acetic acid (117), nitrobenzene (110), or 6 N H_2SO_4 (117); in MeOH (111) and in EtOH (111) (112) the only reaction is esterification (see below)].

The decompn. of C̄ into $CHCl_3$ + CO_2 by boiling with aq. or aq. alk. has long been known (90) (113) (114) (115), and KCN behaves similarly (116). — [For studies on kinetics of decompn. of C̄ in aq. at various temps. see (4) (118) (119) (103) cf. (120); note that rate of decompn. is catalyzed by light (111) (119) (121) (122). — For studies of decompn. of aq. solns. of various salts (117) (123) (124) (125) and influence of light (126) (127) or of presence of various other inorganic salts (128) see indic. refs. — For studies of decompn. of C̄ in aqueous dioxane see (129). — Note that C̄ with $Ca(OH)_2$ on htg. gives $CHCl_3$ and that this reaction has been patented (134).]

[For study of decompn. of C̄ in aniline (117) (111) (130) (131) including influence of supersonic waves (132) see indic. refs.; for decompn. of C̄ in tertiary bases such as dimethylaniline see (133) but note in C̄ does not decompose in pyridine (111).]

[C̄ on htg. in resorcinol or cresol gives (135) $CHCl_3$ + CO_2, but C̄ on htg. in phenol or thymol decomposes differently yielding (135) (136) phosgene (3:5000) + HCl + CO.]

[Note that, as a consequence of the decompn. of C̄ into $CHCl_3$ + CO_2, it has been employed in Reimer-Tiemann types of condensation: e.g., C̄ with phenol + aq. NaOH gives o-hydroxybenzaldehyde (1:0205) + p-hydroxybenzaldehyde (1:0060) (137) (138); many other phenols have also been studied (137) (138).]

Acid Strength of C̄

C̄ in aq. soln. behaves as an exceedingly strong monobasic acid; Neut. Eq. = 163.4 (found 164.6 (91)). — [Ionization constant of C̄ in aq. soln. at 25° is about 1.2 (139) cf. (140), but because of strength of C̄ and its tendency to decompn. (see above) no accurate value is available (143). — For discussion of resonance and acid strength of C̄ see (141) (142) (143). — For studies of electrical conductivity of C̄ in aq. solns. at various temps. see (144) (145) (146) (147) (30).]

[Studies of acid strength of C̄ in nonaqueous solvents include the following: in EtOH (148) (149), in n-BuOH (150) (13), in ether (151), in $CHCl_3$ (151), in formamide (152), in C_6H_6 (153), in chlorobenzene (154), or in dioxane (155). — For study of electrometric titration of C̄ in C_6H_6 (156), in ethylene glycol monomethyl ether ("methylcellosolve") (157), in anisole-n butyl alc. (157), see indic. refs. — For titration of C̄ in Ac_2O soln. with NaOAc see (158) cf. (310). — For study of behavior of C̄ with indicators in C_6H_6 soln. see (159) (160).]

Catalytic Effect of C̄ on Various Reactions

The catalytic influence of C̄ upon diversified types of chem. reactions has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies on catalytic effect of C̄ upon the inversion of l-menthone to d-isomenthone in C_6H_6 (161) (162) or in chlorobenzene (163); upon racemization of methyl-phenyl-acetophenone and of isobutyl-phenyl-acetophenone in various solvents (164); of isopulegone to pulegone in nonaqueous solvents (165); or on hydrogen disproportionation of d-limonene (311), see indic. refs.]

[For studies of catalytic effect of C̄ upon the hydrolysis of EtOAc (144) or of sucrose (166) (167) see indic. refs.]

[For studies of catalytic effect of C̄ upon formn. of ether from EtOH (168); upon rate

of esterification of various org. acids in MeOH (169) or in EtOH (170); upon nitration of toluene (171) cf. (172); upon decompn. of ethyl diazoacetate in C_6H_6 (162) or other solvents (173) (174) (175); upon decompn of nitramide in iso-AmOH (176); upon rearr of N-chloroacetanilide (177); upon rearr. of N-bromoacetanilide in chlorobenzene (178) (179) or in other solvents (179); upon rearr. of N-bromobenzanilide in chlorobenzene (180), upon chromate or perchlorate oxidn. of EtOH (181); upon addition of HBr to 3-methylbutene-1 (182), see indic. refs.

Salts of $\bar{C}$

This topic cannot here be treated exhaustively but the following examples are cited.

Salts with inorganic bases. [$NH_4\bar{A}$, prepn. (183), $NH_4\bar{A}$ $\bar{C}$ (184) (185); $2NH_4\bar{A}.5H_2O$ (186). — Hydroxylamine salt, $HONH_3\bar{A}$, cryst. from dry ether by pptn with lgr., m.p. 133–134° (187).]

[$Li\bar{A}$, n_D^{18} of aq. solns. (8), nonhygroscopic cpds. with betaine or pyridine betaine (188); $Li\bar{A}.2H_2O$ (189), *conductivity of aq. solns* (190). — $Na\bar{A}$ (198), effect of dry distillation (191), conductivity in aq. (190) (192), in dry MeOH (193), in dry EtOH (194); n_D^{18} of aq. solns. (8); $Na\bar{A}.3H_2O$ (196). — $K\bar{A}.H_2O$ (189) (198), solubility and decompn. (197); $K\bar{A}.C$ (184) (185).]

[$Ag\bar{A}$, spar. sol. aq., darkens in air; on dry htg decomposes above 80° (199) yielding (198) AgCl, CO, CO_2, and trichloroacetic acid anhydride (3 6575); with boilg. aq. $Ag\bar{A}$ yields (198) AgCl, CO, CO_2, $CHCl_3$ (3:5050), and $\bar{C}$, for behavior of $Ag\bar{A}$ with I_2 in C_6H_6 see (200). — $Hg\bar{A}$, ndls. from aq in which it is spar sol. (201) (202) (203) (209) (note that it is soluble in C_6H_6 (202)). — $Hg\bar{A}_2$, attempts to prepare this mercuric salt have been unsuccessful (201) (204); aq. solns. of $\bar{C}$ react with HgO long after theoretical amt. has been used (201), and CO, CO_2, and $CHCl_3$ are also formed (205)]

[$Mg\bar{A}_2.4H_2O$ (189). — $Ca\bar{A}_2.6H_2O$ (196); $Ca\bar{A}_2.3\frac{1}{2}H_2O$, eas. sol. (198). — $Sr\bar{A}_2.6H_2O$ (196). — $Ba\bar{A}_2.6H_2O$ (196); $Ba\bar{A}_2.2H_2O$ (206) — $Be\bar{A}_2.2H_2O$ (207) (206). — $Cd\bar{A}_2$ (208); $Cd\bar{A}_2.1\frac{1}{2}H_2O$ (217). — $Zn\bar{A}_2.6H_2O$ (209) — $Pb\bar{A}_2.\frac{1}{2}H_2O$ (210); $Pb\bar{A}_2.H_2O$ (83) — $Cu\bar{A}_2.6H_2O$ (83) (could not be confirmed (201) (211)), $Cu\bar{A}_2.4H_2O$ (211); $Cu\bar{A}_2.3H_2O$ (201) (complexes with benzylamine (212)); $Cu\bar{A}_2.2H_2O$ (complexes with various amines (213)); $Cu\bar{A}_2$ (201) (complexes with various amines (213) (214)), electrolysis (215), electrometric titration (216).]

[$Mn\bar{A}_2.3\frac{1}{2}H_2O$ (217). — $Co\bar{A}_2.4H_2O$ (218) (complexes with various amines (218) (219)); $Co\bar{A}_2.3\frac{1}{2}H_2O$ (217). — $Ni\bar{A}_2.4H_2O$ (189) (218) (complexes with NH_3 (211) and various amines (220)).]

Salts with organic bases. [*Aniline trichloroacetate*, from $\bar{C}$ (1 mole) + aniline (1 mole) in C_6H_6 (223) (224), *or without solvent* (225), *or in aq* (226); *this salt has no true m.p.* (224) although various values ranging from 145° (226) to 163° (225) have been reported. — Note that, although action of heat would be expected to cause loss of H_2O giving ω,ω,ω-trichloroacetanilide (see below), no actual study has been reported. — Note that $\bar{C}$ + aniline + Cu powder in C_6H_6 soln. gives dichloroacetic acid (3 6208) (75–85% yield (223) cf. (227)). — Note finally the existence of *an acid salt of $\bar{C}$ with aniline*, m p. 107–108° (224), from $\bar{C}$ (2 moles) with aniline (1 mole). — *o-Toluidine trichloroacetate;* the prepn. of this salt, m p. 167–168° dec (225), has been claimed (225) but could not be confirmed (224) (228); no other record of it can be found — *p-Toluidine trichloroacetate;* the prepn. of this salt, m p. 135° dec. (225), has been claimed (225) but could not be confirmed (224) (228); *no other record of it can be found — N-Methylaniline trichloroacetate:* m p. 97° (228)]

o-Phenylethylamine trichloroacetate: unreported. — *Benzylamine trichloroacetate:* from $\bar{C}$ + benzylamine in EtOAc, m.p. 118.8–119 8° u c , 120 3–121.3° cor. (229) (note that this

m.p. is practically identical with corresp. benzylamine salt of chloroacetic acid (3:1370) q.v.). — *Piperazine bis-(trichloroacetate)*, m.p. 121.0–121.5° cor. (230). — *Semicarbazide trichloroacetate:* m.p. 154° dec. (231).

[*Phenylhydrazine trichloroacetate:* from C̄ with phenylhydrazine in C_6H_6, m.p. 123° (232). (Note that this product is definitely the salt since on titration with alk. it gives Neut. Eq. 204.7 as against a calcd. value of 202.6 (232); this salt upon htg. would be expected to lose H_2O giving trichloroacetophenylhydrazide, but this product is unreported.)]

[For salts of C̄ with *o*-, *m*-, and *p*-phenylenediamines see (233).]

Behavior of C̄ with Metals

[C̄ with aq. + Zn wool (102), or C̄ with Cu powder in aq. or C_6H_6 (223) (103) (227), gives dichloroacetic acid (3:6208) q.v. — C̄ in conc. NH_4OH dissolves Cu, Zn, or Cd with strong evoln. of ht. but does not attack Ag (234)]

Esterification of C̄

This book includes the following esters of C under their own individual numbers, q.v.: *methyl trichloroacetate* (3:5800), *ethyl trichloroacetate* (3:5950), *n-propyl trichloroacetate* (3:6135), *isopropyl trichloroacetate* (3:5975), *n-butyl trichloroacetate* (3:6315), *isobutyl trichloroacetate* (3:6140), *sec-butyl trichloroacetate* (3:9372), *ter-butyl trichloroacetate* (3:0138), *n-amyl trichloroacetate* (3:6560), *isoamyl trichloroacetate* (3:6490), *ter-amyl trichloroacetate* (3:6185), *trichloromethyl trichloroacetate* (3:0290), *β-chloroethyl trichloroacetate* (3:6510), and *β-methoxyethyl trichloroacetate* (3:9250).

[For studies on esterification of C̄ under various conditions with MeOH (1:6120) (235) (236), with EtOH (1:6130) (235) (237) (238) (239) (240) (241) (242) (243) (244) (20), with *n*-propyl alc. (1:6150) (245), with isopropyl alc. (1:6135) (245) (246) (238), with *n*-butyl alc. (1:6180) (247) (248), with isobutyl alc. (1:6165) (247) (248) (83), with *sec.*-butyl alc. (1:6155) (247), with *ter*-butyl alc. (1:6140) (238), with *n*-amyl alc. (1:6205) (248), with pentanol-2 (1:6185) (248), with pentanol-3 (1:6175) (248), with *ter*-amyl alc. (1:6160) (248), with neopentyl alc. (1:5812) (249), with methyl-vinyl-carbinol (250), with benzyl alc. (1:6480) (238) (251), with diphenylcarbinol (1:5960) (238), with triphenylcarbinol (1:5985) (238), see indic. refs.]

[For study of equilibrium of transesterification with MeOAc (1:3005) or with EtOAc (1:3015) at 30° see (21).]

Addition Reactions of C̄ with Organic Compounds

Addition to unsaturated linkages. C̄ in pres. of suitable catalysts adds to unsatd. linkages giving the corresp. esters [e g., C̄ with propylene + BF_3 gives (48 8% yield (246)) isopropyl trichloroacetate (3:5975); C̄ with trimethylethylene (2-methylbutene-2) (1:8220) gives both *ter*-amyl trichloroacetate (3:6185) and methyl-isopropyl-carbinyl trichloroacetate (for extensive studies of this reaction see (252) (253) (254) (255) (256) (257) (258) (259) (260))].

[C̄ with acetylene + $HgSO_4$ at 60–80° gives (261) vinyl trichloroacetate [Beil. II_1-(94)], b.p. 149° at 760 mm.]

Addition to epoxy compounds. [C̄ with ethylene oxide (1:6105) in cold gives (28% yield (262)) (263) (264) ethylene glycol (mono)trichloroacetate (*β*-hydroxyethyl trichloroacetate) (3:9099). — For behavior of C̄ with 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) see (264).]

Conversion of $\bar{C}$ to Corresponding Acid Halides

[The corresponding trichloroacetyl fluoride is unreported.]

[$\bar{C}$ with PCl_5 (266) (268) (269), with PCl_3 + $ZnCl_2$ (25% yield (270)), with $SOCl_2$ (yield 12% (270), 30% (271)) in C_6H_6 (60% yield (272)) or in pyridine (90% yield (273)), with P_2O_5 + HCl gas (274), with benzotrichloride (3:6540) + $ZnCl_2$ at 100° (77% yield (275)), or with benzoyl chloride (3:6240) (51–56% yield (276)) gives trichloroacetyl chloride (3:5420). — Note also that $\bar{C}$ on pyrolysis at 300° decomposes (100) with formn. of CO_2 + CO_2 + trichloroacetyl chloride (3:5420) + HCl.]

[$\bar{C}$ with PBr_3 gives (265) (266) trichloroacetyl bromide, b.p. 143° (266), 139.5–140° (265); this product is also obtd. from trichloroacetyl chloride (3:5420) with HBr gas at −5° (70% yield (267)).]

[$\bar{C}$ with PI_3 (266) (or better trichloroacetyl chloride (3:5420) with HI at −5° (277)) gives (71.5% yield (277)) trichloroacetyl iodide, b p 74.0–74.2° at 30 mm. (277).]

Conversion of $\bar{C}$ to Corresponding Anhydride

[$\bar{C}$ with P_2O_5 at 200–215° (278) (279), or Na$\bar{A}$ with SO_2Cl_2 (or SO_2 + Cl_2) in EtOAc (280), or $\bar{C}$ with trichloroacetyl chloride (3:5420) and PCl_3 (281), P_2O_5 (282), or $AlCl_3$ (283) gives (yields: 90–95% (280), 80% (278)) trichloroacetic acid anhydride (3:6575).]

Ⓟ **Color test with NH_4OH/Cu_2Cl_2 reagent.** $\bar{C}$ on shaking in filled stoppered bottle with conc. aq. NH_4OH contg Cu_2Cl_2 gives dark blue color instantly (284); note, however, that very similar behavior is shown by dichloroacetic acid (3:6208).

—— **Methyl trichloroacetate:** oil, b.p. 153° (see 3.5800).

—— **Ethyl trichloroacetate:** oil, b p. 167° (see 3:5950).

—— **Phenyl trichloroacetate:** oil, b p. 254–255° dec. (135). [From trichloroacetyl chloride (3:5420) with sodium phenolate in pet. ether (135).] [Note that the isomeric 4-(trichloroacetyl)phenol, m.p. 99 0–99.5° has been prepd. indirectly from trichloroacetonitrile + phenol + $AlCl_3$ (285).]

—— **o-Tolyl trichloroacetate:** unreported [Note, however, that the isomeric 4-(trichloroacetyl)-2-methylphenol, m.p. 90–91°, has been obtd. indirectly (285).]

—— ***m*-Tolyl trichloroacetate:** unreported. [Note, however, that both the isomers, viz., 4-(trichloroacetyl)-3-methylphenol, m.p. 83–87°, and 6-(trichloroacetyl)-3-methylphenol, oil, have been obtd. indirectly (285).]

—— ***p*-Tolyl trichloroacetate:** m.p. 68–69° (285). [Obtd only by indirect means (285).]

—— **Benzyl trichloroacetate:** oil, b p 178 5° at 50 mm (286), 148–149° at 15 mm. (264), D_4^4 = 1.3887 (286), $n_D^{18.8}$ = 1.5288 (286). [From $\bar{C}$ with benzyl alc. (1:6480) + HCl gas at 100° (286), or from trichloroacetyl chloride (3:5420) with benzyl alc (1:6480).]

—— ***p*-Nitrobenzyl trichloroacetate:** m p. about 80° cf. (287). [Unsuitable as Ⓓ (287).]

—— **Phenacyl trichloroacetate:** unreported.

—— ***p*-Chlorophenacyl trichloroacetate:** unreported.

—— ***p*-Bromophenacyl trichloroacetate:** unreported.

—— ***p*-Iodophenacyl trichloroacetate:** unreported.

—— ***p*-Phenylphenacyl trichloroacetate:** unreported.

Ⓓ ***S*-Benzylthiuronium trichloroacetate:** m p 148–149° (288). [Note that for corresp. salts from chloroacetic acid (3:1370) and from dichloroacetic acid (3:6208) m.p. values are respectively 159–160° and 178–179° (288).]

Ⓓ ***S*-(*p*-Chlorobenzyl)thiuronium trichloroacetate:** m.p. 148° cor. (289). [From $\bar{C}$ (as Na$\bar{A}$) with *S*-(*p*-chlorobenzyl)thiuronium chloride (289) (m.p. 197°) in alc. (289); note that corresp deriv. of chloroacetic acid (3:1370) has m.p. 158° cor. (289).]

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[illegible] (2) **88**, 342–357
[illegible] (207) Parsons,
[illegible] **35**, 371 (1935).
[illegible] ckh, *Ann.* **210**,
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[illegible] (212) Ablov, *Bull. soc.*
[illegible] (214) Costachescu,
[illegible] 2647 (1933). (215)
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[illegible] *Cent.* **1930**, II 227;
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). (234)

hem. Soc.

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(1939). (268) Del

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U.S. 1,71

Chem. So

(286) Se

(288) Ve

Chem. So

(291)

(293) Ca

108 (191

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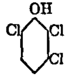
3:1160 2,3,6-TRICHLOROPHENOL



$C_6H_3OCl_3$ Beil. VI - 190
VI_1—
VI_2-(180)

M.P. 58° (1) (2)
55° (4)
53–54° (5) (6)

B.P. 252–253° u.c. (5)
248.5–249.5° (6)

Ndls. (from alc.) with intense and persistent phenolic odor. — Somewhat sol. in hot aq.; volatile with steam. — Eas. sol. alc., ether, lgr., AcOH; sol. hot C_6H_6 but ppts. on cooling.

[For prepn. from 2,3,6-trichloro-4-aminophenol via diazo reactn. see (3).]

$\bar{C}$ is strongly acidic; ionization const. at 25° is 7.3×10^{-7} (2); $\bar{C}$ dissolves in Na_2CO_3 or NaOH (5); $\bar{C}$ can be titrated with $N/10$ alk.; Neut. Eq. = 197.5 (1) (4).

$\bar{C}$ in AcOH, treated with 1.4 moles Br_2, poured into aq. yields 4-bromo-2,3,6-trichlorophenol, ndls. from AcOH, m.p. 80° (3). [The methyl ether of this prod. has m.p. 69–70°; the benzoate, m.p. 110° (3).]

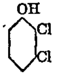
$\bar{C}$ treated with 1.5 moles Br_2 without solvent yields (3) 4,5-dibromo-2,3,6-trichlorophenol, ndls. from dil. AcOH, m.p. 205° (3). [The methyl ether of this prod. has m p. 130°; the benzoate, m.p. 153° (3).]

$\bar{C}$ treated with $(CH_3)_2SO_4$ + 20% KOH at 100° for an hour yields its own methyl ether, 2,3,6-trichloroanisole, b.p. 227–229° at 756 mm.; pr. from alc., m.p. 45° (3).

Ⓓ **2,3,6-Trichlorophenyl benzoate**: from $\bar{C}$ + BzCl + 10% KOH; cryst. from pet. ether/lgr., m.p. 92–93° (3); from alc., m.p. 90° (4).

3:1160 (1) Tiessens, *Rec. trav. chim.* **50**, 113–114 (1931). (2) Tiessens, *Rec. trav. chim.* **48**, 1066–1068 (1929). (3) Kohn, Fink, *Monatsh.* **56**, 139–141 (1930). (4) Holleman, *Rec. trav. chim.* **39**, 742–743 (1920). (5) Lampert, *J. prakt. Chem.* (2) **33**, 376–378 (1886). (6) Hirsch, *Ber.* **13**, 1908 (1880).

3:1175 2,3-DICHLOROPHENOL



$C_6H_4OCl_2$ Beil. VI —
VI_1-(102)
VI_2—

M.P. 58° (1)
56–57° (2) (3)

B.P. 206° (1)

Cryst. (from pet. eth. (3)). — $\bar{C}$ mixed with 2,5-dichlorophenol (3:1190), m p. 57°, depresses m.p. (2). — $\bar{C}$ is extraordinarily volatile; if dried in vac. this leads to substantial

losses; the volatility and intense odor of C̄ differentiate this dichlorophenol from its isomerides (2). — Odor resembles that of o-chlorophenol and iodoform (3). — C̄ is volatile with steam (3).

[For prepn. from 3-amino-2-chlorophenol via Sandmeyer method see (2) (4); from 2,3-dichloroaniline via diazo reaction see (3); from barium 2,3-dichlorophenol-4,6-disulfonate by hydrolysis of sulfonic acid groups with steam (70% yield) see (1).]

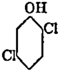
[For data on dissociation constant see (5).]

C̄ on direct bromination (1) yields 4,6-dibromo-2,3-dichlorophenol, colorless ndls. (rapidly becoming opaque) from AcOH (1), or colorless feathery ndls. from alc. (4), m p. 90° (1) (4). [The methyl ether of this product, 4,6-dibromo-2,3-dichloroanisole, long needle-like pr. from alc., has m.p. 82° (1).]

C̄ dislvd. in aq. NaOH and shaken with $(CH_3)_2SO_4$ yields (3) the methyl ether, 2,3-dichloroanisole, m.p. 31° (3).

3:1175 (1) Hodgson, Kershaw, *J. Chem. Soc.* **1930**, 1423. (2) Henley, Turner, *J. Chem. Soc.* **1930**, 940 (3) Holleman, *Rec trav. chim.* **37**, 101–104 (1918). (4) Hodgson, Smith, *J. Chem. Soc.* **1931**, 2271. (5) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935).

3:1190 2,5-DICHLOROPHENOL



$C_6H_4OCl_2$ Beil. VI - 189, VI_1-(103), VI_2-(178)

M.P. 58° (1) (2) (3) (4); 59° (5) B.P. 211° at 744 mm. (1) (4); 94° at 14 mm. (3)

Cryst with strong and persistent phenolic odor. — Spar. sol. aq., eas. sol. alc., ether, C_6H_6 — Volatile with steam.

[For prepn. from 2,5-dichloroaniline [Beil. XII-625] via diazo reaction (90% yield (1); 86% yield (6); 70% yield (5)) see (1) (6) (5) (2); from 1,2,4-trichlorobenzene + $NaOCH_3$ in MeOH at 180° see (7)]

C̄ in dil. alc. reddens blue litmus, dec. on boilg. with Na_2CO_3 Gives only faint color with $FeCl_3$ (1). [For study of ionization const. see (11)]

C̄ dislvd. in 3 pts. $CHCl_3$ and shaken with conc. HNO_3 gives on cooling $CHCl_3$ 80% yield of 2,5-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from pet ether, m p. 117° (8). [Further nitration yields 2,5-dichloro-4,6-dinitrophenol, yel. pr.. m p. 146° (8).] — C̄ htd. with conc. H_2SO_4 + fumg. H_2SO_4, then nitrated as specified (9), yields 2,5-dichloro-6-nitrophenol, volatile with steam, yel. pr. from pet. eth., m p. 70° (9).

C̄ in AcOH treated with 2 moles Br_2, poured into aq., gives (100% yield (6)) 2,5-dichloro-4,6-dibromophenol, ndls. from dil. AcOH, m.p. 100.5° (6), 99–100° (10). [This dibromo compd. results also from C̄ in AcOH + NaOAc + *1* mole Br_2 on htg. at 100° (10).] [C̄ with Fe + excess Br_2 gives (100% yield (6)) 2,5-dichloro-3,4,5-tribromophenol, ndls. from AcOH, m p. 206° (6).]

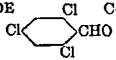
C̄ dislvd. in KOH and shaken with $(CH_3)_2SO_4$ yields the methyl ether, 2,5-dichloroanisole, b p 225–227° u c. at 752 mm. (6), b p. 140° at 40 mm. (2), m p. 24° (5) (2).

Ⓓ 2,5-Dichlorophenyl benzoate: from C̄ + aq. KOH + BzCl, ndls. from 96% alc., m p. 69° (6).

3:1190 (1) Noelting, Kopp, *Ber.* **38**, 3510 (1905). (2) Holleman, *Rec. trav. chim.* **37**, 101–104 (1918). (3) Kohlrausch, Stockmair, Ypsilanti, *Monatsh.* **67**, 90 (1936). (4) Ger. 349,794, March 9, 1922; *Cent.* **1922**, IV 45. (5) de Crauw, *Rec. trav. chim.* **50**, 770 (1931). (6) Kohn, Fink, *Monatsh.* **58**, 78–83 (1931). (7) Holleman, *Rec. trav. chim.* **37**, 201 (1918). (8) Fries, *Ann.* **454**,

247 (1927). (9) Hodgson, Kershaw, *J. Chem. Soc.* **1929**, 2922–2923. (10) Fox, Turner, *J. Chem. Soc.* **1930**, 1860.
(11) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935).

3:1200 2,4,6-TRICHLOROBENZALDEHYDE



$C_7H_3OCl_3$ Beil. VII-238
VII_1—

M.P. 58–59° (1) (2)

Cryst. from lgr.

[For prepn. of C̄ from 2,4,6-trichlorobenzal (di)chloride (3:0142) by hydrolysis with fumg. H_2SO_4 (94% yield) see (1); for prepn. of C̄ from 4-amino-2,6-dichlorobenzaldehyde by diazotization and use of Cu_2Cl_2 reaction see (1).]

[C̄ on oxidn. with $KMnO_4$ should yield 2,4,6-trichlorobenzoic acid (3:4545), m.p. 164°, but this reaction is not actually reported in the literature.]

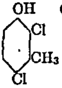
C̄ with 50% aq. KOH or 50% aq. NaOH at 100° undergoes cleavage of the aldehyde group giving (yields: 89% and 74% respectively) 1,3,5-trichlorobenzene (3:1400), m.p. 63°, accompanied by the corresp. potassium formate (1).

[C̄ with MeMgI in dry ether, followed by usual hydrolysis, gives (93% yield (3)) methyl-2,4,6-trichlorophenyl-carbinol, ndls. from lgr., m.p. 76.5°, b.p. 158–163° cor. at 17 mm.]

—— 2,4,6-*Trichlorobenzaldoxime*: unreported.
—— 2,4,6-Trichlorobenzaldehyde phenylhydrazone: unreported.
—— 2,4,6-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.
—— 2,4,6-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:1200 (1) Lock, *Ber.* **66**, 1532 (1933). (2) Geigy & Co. Ger. 199,943, July 4, 1908; *Cent.* **1908**, II 363–364; [*C.A.* **2**, 3000 (1908)]. (3) Lock, Böck, *Ber.* **70**, 924 (1937).

3:1205 2,4-DICHLORO-3-METHYLPHENOL
(2,4-Dichloro-*m*-cresol.)



$C_7H_6OCl_2$ Beil. VI —
VI_1—
VI_2-(*356*)

M.P. 58–59°	**(1)**	**B.P. 235–236°**	**at 745 mm.**	**(2)**
58°	**(2)**	**234°**		**(1)**
		75–80°	**at 4 mm.**	**(1)**

Note that the products of m.p. 44° (3), 45° (4), and 46° (5) formerly supposed to have been C̄ are now regarded (1) as 2,4,6-trichloro-3-methylphenol (3:0618).

[For prepn. of C̄ from 2-chloro-3-methylphenol (*3:1055*) or from *4-chloro-3-methyl*phenol (3:1535) in cold $CHCl_3$ with Cl_2 see (1); from 3-methylphenol (*m*-cresol) (1:1730) in $CHCl_3$ with 2 moles Cl_2 (other isomers are also formed) see (1); from 3-methylphenol-sulfonic acid-4 (2) in nitrobenzene solution with Cl_2 (other products are also formed) see (2).]

C̄ in $CHCl_3$ gives with Cl_2 (1 mole) alm. quant. yield (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

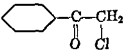
C̄ in $CHCl_3$ gives with Br_2 (1 mole) (1) 2,4-dichloro-6-bromo-3-methylphenol, m.p. 58–59° (1).

Ⓓ 2,4-dichloro-3-methylphenyl benzoate: fine plates from alc., m.p. 78–78.5° (1) [From C̄ with BzCl in pyridine (1).]

Ⓓ 2,4-Dichloro-3-methylphenyl benzenesulfonate: fine ndl.-like pl. from alc., m p 69.5° (1). [From C̄ with benzenesulfonyl chloride in pyridine (1).] [Note the proximity of the m.p. of this deriv. to that of the corresp. deriv. of 2,6-dichloro-3-methylphenol (3:0618).]

Ⓓ 2,4-Dichloro-3-methylphenyl *p*-toluenesulfonate: shiny pl. from alc., m.p. 100–101° (1). [From C̄ with *p*-toluenesulfonyl chloride in pyridine (1).]

[illegible] 4216–4218 (1933). (2) Huston, Neely, *J. Am* [illegible] kawa, Sakamoto, *J. Chem. Soc. Japan* **51**, 275– [illegible] ta, Mitter, *J Am. Chem. Soc.* **41**, 2033 (1919). (5) Claus, Schweitzer, *Ber.* **19**, 930 (1886).

3:1212 PHENACYL CHLORIDE  C_8H_7OCl Beil. VII - 282
(α-Chloroacetophenone, VII₁-(151)
ω-chloroacetophenone,
chloromethyl phenyl ketone)

M.P.		B.P.		
[60°	(1)]	244–245°	u.c.	(6)
59°	(2)	244°		(37)
58–59°	(3) (4) (5) (6)	241–242°		(36)
58.8°	(7)	140°	at 15 mm.	(1)
58.5°	(8)	139–141°	at 14 mm.	(3)
57–58°	(9) (71)	120.0–120.2°	at 10 mm.	(12)
57°	(10) (11)	120–125°	at 4 mm.	(15)
56.5–56.8°	(12)			
56.5°	(13) (14)			
56–57°	(15) (64)			
56°	(16) (36)			
55–55.5°	(17)			
55°	(37)			
54.5°	(18) (154)			
54°	(31)			

Colorless tbls. from dil. alc. or lgr. — Vapors of C̄ are very strongly lachrymatory (see also below). — C̄ is insol. aq. but volatile with steam; C̄ is eas sol alc., ether, or C_6H_6.

[For study of soly. of C̄ in EtOH, C_6H_6, CCl_4, or acetophenone over range −23.5° to 53 5° see (19): note that C̄ with C_6H_6 (1:7400) gives (19) a eutectic, m.p −1.6°, contg. 76 wt. % C̄; C̄ with acetophenone (1:5515) gives a eutectio, m p. +5.9°, contg 70 wt. % C̄ (19).]

USES OF C̄

In addn. to its uses as a chem. intermediate, C̄ because of its irritant and lachrymatory properties has been much studied as a chemical warfare agent and tear gas under the arbitrary designation "CN."

[For general surveys from this viewpoint see (20) (21). — C̄ is sol. in many org solvents and is frequently loaded into grenades and shells in such solutions of which three common examples are "CNB" (consisting of C̄ + C_6H_6 + CCl_4), "CND" (consisting of C̄ + ethylene dichloride (3:5130)), and "CNS" (consisting of C̄ + $CHCl_3$ + nitrochloroform = chloropicrin). — For examples of patents on these and other types of tear-gas cartridges and munitions contg. C̄ see (23) (24) (25) (26) (27); for use of C̄ as insecticide see (28).]

[For dispensing apparatus for C̄ (29) or for mill for disintegration of C̄ (30) see indic. refs.]

[For m.p./compn. diagram of system $\bar{C}$ + "Adamsite" (10-chloro-9,10-dihydrophenarsazine), eutectic, m.p. 50°, contg. 90 mole % $\bar{C}$, see (31).]

[For studies of effect of $\bar{C}$ on skin see (32) (33) (34); for contamination of food by $\bar{C}$ see (35).]

PREPARATION OF $\bar{C}$

From chloroacetyl chloride with benzene. [For prepn. of $\bar{C}$ from chloroacetyl chloride (3:5235) with C_6H_6 + $AlCl_3$ (yield 85–88% (15) (64)) (2) (14) (36) (71) see indic. refs.]

From acetophenone. [For prepn. of $\bar{C}$ from acetophenone (1:5515) with Cl_2 in AcOH (4) (18), in CS_2 (85% yield (37)), in lgr. (38) or directly without solvent (yields 65% (6) (37)) (39) see indic. refs.; from acetophenone (1:5515) by electrolysis of its soln. in HCl (40), or by *chlorination* with aq. *N*-chlorourea (41), see indic. refs.]

From benzoyl chloride with diazomethane. [For formn. of $\bar{C}$ from benzoyl chloride (3:6240) with diazomethane in ether (72% yield) see (3); note, however, that this procedure has subsequently been much disputed, and for discussion see also (42) (43) (44) (45) (46) (47) (48).]

From miscellaneous sources. [For prepn. of $\bar{C}$ from *N*-(α,β-dichlorovinyl)diethylamine (yield 92.6% (49)), from chloroacetonitrile (50), or for possible formn. from chloroacetic acid (3:1370) (51), all with C_6H_5MgBr, see indic. refs.; for formn. of $\bar{C}$ from phenyl copper (52), from phenyldichloroarsine (yields: 58.5% (53), 55% (54)) (55), all with chloroacetyl chloride (3:5235), see indic. refs.; for formn. of $\bar{C}$ from 1-chloro-2-phenylpropanol-2 (styrene chlorohydrin) (3:9570) by oxidn. with $K_2Cr_2O_7/H_2SO_4$ (1) or from diphenacyltelluride dichloride by oxidn. with $KMnO_4$ (5) see indic. refs.; for formn. of $\bar{C}$ from benzalacetophenone (chalcone) (1:5155) by actn. of Cl_2 in *ter*-butyl alc. (other prods. are also formed) see (17).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction

No authentic studies on reduction of $\bar{C}$ appear to be reported.

Oxidation

$\bar{C}$ on oxidn. with CrO_3 (39), or $K_2Cr_2O_7$ + H_2SO_4 (58) (13) gives benzoic acid (1:0715). — $\bar{C}$ also reduces $NH_4OH/AgNO_3$ (13) [perhaps because of some hydrolysis to ω-hydroxyacetophenone (1:5180)].

Halogenation

Chlorination. [$\bar{C}$ on further chlorination under conditions favoring side-chain substitution would be expected to yield ω,ω-dichloroacetophenone (3:6835) and ultimately ω,ω,ω-trichloroacetophenone (3:6874), but no authentic record that this has actually been achieved can be found.]

Bromination. [$\bar{C}$ with Br_2 under suitable conditions gives (56) ω-bromo-ω-chloroacetophenone, m.p. 37–37.5°, b.p. 133–134° at 7.5 mm. (56). — $\bar{C}$ in AcOH + NaOAc with Br_2 as directed (57) gives a mixt. consisting of 30% ω,ω-dibromo-ω-chloroacetophenone + 70% ω,ω,ω-tribromoacetophenone.]

Nitration. $\bar{C}$ in conc. H_2SO_4 at −20° treated as directed (9) with a mixt. of fumg. HNO_3 (D = 1.50) + conc. H_2SO_4 gives (77% yield (9)) *m*-nitrophenacyl chloride, m.p. 103° (59), 102–103° (16), 100.5–102° (9). — [Note that the other two isomeric mononitrophenacyl chlorides, viz., *o*-nitrophenacyl chloride, m.p. 66–67° (60) (61), and *p*-nitrophenacyl chloride, m.p. 107° (62), are also known, but prepd. indirectly; note also that no dinitration prods. of $\bar{C}$ are known.]

Behavior of $\bar{C}$ with Other Inorganic Reactants

With water. [$\bar{C}$ does *not* readily hydrolyze with aq. but on protracted boilg. (e g , 20 hrs. (63)) with a large vol. of aq. gives ω-hydroxyacetophenone (1:5180).]

With nitrous acid. $\bar{C}$ with HNO_2 (from *n*-butyl nitrite + HCl gas) in dry ether gives (yields: 85 6% (64), 82–86% (15)) ω-chloro-ω-isonitrosoacetophenone (phenylglyoxylohydroxamyl chloride) [Beil. X-662, X_1-(315)], white ndls. from CCl_4 (64) or from CCl_4 + C_6H_6 (3:1) (15), m.p. 132–133° (15) (64).

With PCl_5. [$\bar{C}$ with PCl_5 on distn. gives (65) α,β-dichlorovinylbenzene (α,β-dichlorostyrene) [Beil. V-477, V_2-(367)], b.p. 221°.]

With various salts of inorganic acids. [$\bar{C}$ with KI (66) (67) or better NaI (38) in alc. gives *ω-iodoacetophenone* (phenacyl iodide) [Beil. VII-286], m p. 30°; for study of rate of reactn. of $\bar{C}$ with KI in acetone at 0° (11) or with NaI or LiI in acetone at 0° or −10° (10) see indic. refs.]

$\bar{C}$ does *not* add $NaHSO_3$ (37). — $\bar{C}$ in alc. with $Na_2S_2O_3$ (2 moles) in aq. refluxed 20 hrs. gives sodium phenacylthiosulfate which with HCl gives (73% yield (69)) ω-mercaptoacetophenone (phenacyl mercaptan). — $\bar{C}$ with Na_2S in alc. at 60° gives (70) diphenacyl sulfide [Beil. VIII-94, $VIII_1$-(541)], m.p. 76 5–77.2° (70), 76° (147); for use of this reactn. in detn. of $\bar{C}$ see (14).

With ammonia. [$\bar{C}$ with NH_3 (1 mole) would be expected to give ω-aminoacetophenone (phenacylamine) [Beil. XIV-49, XIV_1-(368)], but such direct result has never been reported; note, however, that $\bar{C}$ (1 mole) with hexamethylenetetramine (1 mole) in $CHCl_3$ at room temp. for 12 hrs. gives (60% yield (68)) a 1:1 addn cpd., m p. 145°, which upon alcoholysis with conc. HCl in alc. 3 days in cold gives (63–74% yield (68)) phenacylamine hydrochloride.

[$\bar{C}$ with alc. NH_3 in s.t. at 100° as directed (2) gives a mixt. contg diphenacylamine hydrochloride [Beil. XIV-53, XIV_1-(371)], m.p. 235°, together with the hydrochlorides of 2,5-diphenylpyrazine and 2,6-diphenylpyrazine; for discussion of mechanism see (2).]

Behavior of $\bar{C}$ with Organic Reactants

With Hydrocarbons (+ $AlCl_3$)

$\bar{C}$ with C_6H_6 + $AlCl_3$ *in s.t. at 100° failed to react (71).* — $\bar{C}$ *with toluene (1:7405)* + $AlCl_3$ under reflux gives (71) a prod , m.p 84–85°, which is presumably ω-(*p*-tolyl)acetophenone [Beil. VII-448], although this prod. obtd. by other methods has different consts.

With Organic Hydroxy (or Mercapto) Compounds

With alcohols. [$\bar{C}$ with NaOMe might be expected to yield ω-methoxyacetophenone, b p 228–230° at 760 mm. (72) (73), b p. 118–120° at 15 mm. (72) (73), m.p. 7–7 5° (73) (corresp. semicarbazone, m.p. 85° (72), 129° (73) (note disagreement); corresp. 2,4-dinitrophenylhydrazone, m p. 191–192° (73)); note, however, that no record of this reaction has been reported and the ω-methoxyacetophenone is best prepd. (71–78% yield (74)) from methoxyacetonitrile with C_6H_5MgBr; *note also that* $\bar{C}$ *with alk. reagts. such as NaOMe reacts in an unexpectedly complex manner yielding (153) cyclic " halogen-diphenacyls."*]

[$\bar{C}$ with NaOEt would be expected to yield ω-ethoxyacetophenone [Beil VIII-90], b p. 134–136° at 21 mm. (75), 130° at 15 mm. (76), 120–122° at 15 mm. (77), D_4^{20} = 1.0552 (77), n_D^{20} = 1 5250 (77) (corresp. oxime, m.p. 55° (75); corresp. semicarbazone, m.p. 128° (75)); note, however, that no record of this reactn. has been reported and the ω-ethoxyacetophenone is best prepd. (68% yield (77)) cf. (75) (76) from ethoxyacetonitrile with

C_6H_5MgBr; note also that C̄ with alk. reagts. such as NaOEt reacts in an *unexpectedly* complex manner yielding (153) cyclic "halogen diphenacyls."

[C̄ (1 mole) with ethylene glycol (1:6465) (1 mole) in C_6H_6 contg. trace of benzenesulfonic acid gives on htg. (95% yield (81)) the corresp. cyclic ketal, viz., 2-(chloromethyl)-2-phenyl-1,3-dioxolane, m.p. 67°, b.p. 144–146° at 15 mm. (81).]

With phenols. [C̄ with dry sodium phenolate (78) gives ω-phenoxyacetophenone [Beil. VIII-91], m.p. 74° cor. (79), b.p. 255–257° (78), 187° cor. at 9 mm. (79) (corresp. semicarbazone, m.p. 187.0–187.5° cor. (79)); note, however, that this prod. is best prepd. (45% yield (79)) from phenoxyacetonitrile with C_6H_5MgBr, or from phenoxyacetyl chloride + C_6H_6 + $AlCl_3$ cf. (80).]

With mercaptans. [C̄ with *n*-BuSH in alc. NaOH gives (82) phenacyl *n*-butyl sulfide, b.p. 140° at 3 mm., D_{25}^{25} = 1.0589, n_D^{20} = 1.5050.]

[C̄ with sodium *p*-nitrothiophenate in aq. alc. on htg. gives (98% yield (83)) phenacyl *p*-nitrophenyl sulfide, yel. pl. from 50–80% AcOH, m.p. 118°. — C̄ (1 mole) with sodium *p*-thiocresolate (1 mole) in MeOH boiled several hrs. does *not* give the expected phenacyl *p*-tolyl sulfide, m.p. 37° cf. (101); distillation of the reaction prod. gives (58.5% yield (84)) phenacyl *p*-tolyl sulfoxide, b.p. 182–184° at 5 mm., m.p. 46° accompanied by acetophenone; note that with H_2O_2 this sulfoxide oxidizes to phenacyl *p*-tolyl sulfone, m.p. 110° (see also below).]

Behavior with Carbonyl Compounds

With aromatic aldehydes. [C̄ (1 mole) with benzaldehyde (1½ moles) in alc. with alc. NaOEt (1 mole) in cold condenses with loss of HCl giving (80% yield (85)) α-benzoyl-α′-phenyl-ethylene oxide (benzalacetophenone oxide) [Beil. XVII₁-(196)], colorless cryst. from alc. (85) or from cold acetone by addn. of pet. ether (86), m.p. 89–90° (85) (86); note that this prod. can also be obtd. in other ways, notably from benzalacetophenone (chalcone) (1:5155) with Na_2O_2 + HCl in cold (85% yield (86)) or with H_2O_2 in alk. soln. (90% yield (88)) (87) (89); although *cis* and *trans* stereoisomers are possible, only one form is known.]

[C̄ with *o*-nitrobenzaldehyde in alc. NaOEt (although this particular pair has not actually been reported) should yield similarly α-benzoyl-α′-(*o*-nitrophenyl)ethylene oxide [Beil. $XVII_1$-(197)] since phenacyl bromide behaves (90) in this fashion; note that for this prod. the two expected geom. stereoisomers are both formed, one with m.p. 175°, the other with m.p. 110°.]

[C̄ with *m*-nitrobenzaldehyde in alc. NaOEt (although this particular pair has not actually been reported) should give similarly *α-benzoyl-α′-(m-nitrophenyl)ethylene oxide* [Beil. $XVII_1$-(197)] since phenacyl bromide behaves in this manner (80% yield (91)); one stereoisomer is known, m.p. 118° (91). — Note, however, that C̄ (1 mole) with *m*-nitrobenzaldehyde (1 mole) in AcOH satd. with HCl gas and stood 24 hrs. reacts differently giving (92) *m*-nitrobenzalacetophenone dichloride [Beil. VII_1-(238)], m.p. 148°.]

[C̄ (1 mole) with *p*-methoxybenzaldehyde (anisaldehyde) (1:0240) (1 mole) in alc. NaOEt gives (93) α-benzoyl-α′-(*p*-methoxyphenyl)ethylene oxide, m.p. 87° (93) (89); also obtd. from *p*-methoxybenzalacetophenone (1:9011) with alk. H_2O_2 (89).]

[C̄ (1 mole) + *o*-nitrobenzalacetophenone (1 mole) in acetone/dioxane with alc. NaOEt (1 mole) gives in 15 min. but yield not stated (93) 1,2-dibenzoyl-3-(*o*-nitrophenyl)cyclopropane, m.p. 177° (93).]

Behavior of C̄ with Salts of Organic Acids

C̄ with salts of organic acids gives in general the corresp. phenacyl esters although when the latter are to be prepd. as means of identification of the acids the more reactive phenacyl

bromide is usually employed; for m.p.'s of the phenacyl esters of various acids of Order I see Vol. I, p. 650.

[$\bar{C}$ with KCN in dil. alc. on htg. gives (47% yield (94)) ω-cyanoacetophenone (benzoylacetonitrile) [Beil. X-680, X_1-(322)], m.p. 83° (94), 80–81° (95) (96); this prod. may also be prepd. by other means, e.g., from phenacyl bromide with dil. alc. KCN (60% yield (97)), or from ethyl benzoate with acetonitrile + NaOEt (yields: 60% (96), 56% (95)).]

[$\bar{C}$ with KSCN in MeOH (98) or EtOH (65) gives ω-thiocyanoacetophenone (phenacyl thiocyanate) [Beil. VIII-94], m.p. 74.1–76.6° cor. (98), 74° (99).]

[$\bar{C}$ with sodium p-toluenesulfinate in boilg. alc. gives (100) cf. (101) phenacyl p-tolyl sulfone (ω-(p-toluenesulfonyl)acetophenone), m.p. 110° (100) (see also above for formn. of this prod. from $\bar{C}$ + sodium thio-p-cresolate).]

Behavior of $\bar{C}$ with RMgX Compounds

[$\bar{C}$ (1 mole) with EtMgBr (1 mole) in dry ether gives an addn. prod. which after evapn. of ether, htg. at 130–140°, and hydrolysis gives (yield not stated (102)) benzyl ethyl ketone (1-phenylbutanone-2) [Beil. VII-314, VII_1-(167)], b.p. 222–227° (103), 221–223° (102), 110° at 13 mm. (104) (corresp. semicarbazone, m.p. 156–156.5° cor. (105), 150–153° (103), 153° (106), β-form 152°, α-form 146° (104), 146° (102), corresp. 2,4-dinitrophenylhydrazone, m.p. 140–141° (103)); not rearr. in formn. of this prod. by this method.]

[$\bar{C}$ with n-hexyn-1-yl MgBr in dry ether adds normally and on hydrolysis gives (107) the expected 1-chloro-2-phenylnonyn-3-ol-2.]

Behavior of $\bar{C}$ with Amines

With primary aliphatic amines. [$\bar{C}$ (1 mole) with $MeNH_2$ (2.5 moles) in alc. for 5–6 hrs. in cold gives (108) ω-(methylamino)acetophenone [Beil. XIV-50, XIV_1-(369)] (corresp. $\bar{B}$.HCl (23% yield (108)), m.p. 219° (108)). — $\bar{C}$ with $n\text{-}BuNH_2$ similarly gives (35% yield (108)) ω-(n-butylamino)acetophenone hydrochloride, m.p. 214–215° (108).]

[$\bar{C}$ with β-aminoethanol (ethanolamine) readily gives (109) N-(β-hydroxyethyl)phenacylamine, m.p. 144° (109).]

With primary aromatic amines. [$\bar{C}$ with aniline should yield N-(phenacyl)aniline [Beil. XIV-51, XIV_1-(369)], m.p. 98–99° (110) (corresp. oxime, m.p. 105–106° (111); corresp. semicarbazone, m.p. 171° (110)); however, although the rate of this reaction in abs. alc. at 40° (38) and in 90% alc. at 30.5° (16) cf. (112) has been studied, the usual method of prepn. of N-(phenacyl)aniline is from phenacyl bromide + aniline. — *Pure* N-(phenacyl)aniline, contrary to earlier statements, is remarkably stable and can be exposed to air at room temp. for 18 months or distilled under reduced press. (b.p. 208–210° at 12 mm.) without change (113); for important study of mechanism of conversion of N-(phenacyl)aniline to 2-phenylindole see (113) (114).]

[The behavior of $\bar{C}$ with the three toluidines has not itself been studied but should be similar to that of phenacyl *bromide* which with o-toluidine gives (115) (116) N-(phenacyl)-o-toluidine [Beil. XIV-52, XIV_1-(370)], m.p. 91° (116), 89° (115) (corresp. oxime, m.p. 92° (116)); with m-toluidine gives N-(phenacyl)-m-toluidine, m.p. 110° (117); with p-toluidine gives N-(phenacyl)-p-toluidine [Beil. XIV-52, XIV_1-(370)], m.p. 134° (118), 127° (115) (corresp. oxime in two geom. stereoisomers of m.p. 97° and 92°, resp. (111)).]

With secondary aliphatic amines. [$\bar{C}$ with Me_2NH should yield ω-(dimethylamino)-acetophenone (phenacyl dimethylamine) [Beil. XIV-50], b.p. 126–128° at 18 mm. (119), 122–123° at 14 mm. (120) (corresp. $\bar{B}$.HCl, m.p. 174° (120), corresp. $\bar{B}$.HBr, m.p. 184–186° (121), corresp. $\bar{B}$.PkOH, m.p. 150° (119), 143° (122), 141° (123)); note, however,

that this particular combination of reactants has not actually been reported and that the ω-(dimethylamino)acetophenone is usually obtd. from phenacyl *bromide* with Me_2NH (119) (121), or from dimethylaminoacet-*N*,*N*-dimethylamide with C_6H_5MgBr (80% yield (120) (125)).]

[C̄ (1 mole) with Et_2NH (2 moles) in C_6H_6 stood 2 days at room temp. ppts. $Et_2NH.HCl$ and gives (65% yield (125)) ω-(diethylamino)acetophenone, b.p. 148–152° at 30 mm. (125), $n_D^{23} = 1.5180$ (125).]

[C̄ + *bis*-(β-hydroxyethyl)amine (diethanolamine) in C_6H_6 on long boilg. gives (109) *N*-phenacyl-*N*,*N*-*bis*-(β-hydroxyethyl)amine, m.p. 44° (109).]

With secondary heterocyclic amines. [C̄ with piperidine in dry ether splits out HCl and yields (126) ω-(piperidino)acetophenone (*N*-(phenacyl)piperidine) [Beil. XX-42], b.p. 180–181° cor. at 26 mm. (127), 157° at 15 mm. (128), 163–164° at 13 mm. (126), $D_4^{21.2} =$ 1.0430 (126), $n_D^{22.4} = 1.5408$ (126) (corresp. B̄.HCl, m.p 226–227° (129), corresp. B̄.HBr, m.p. 227–228° (135), corresp. oxime, m.p. 112–115° (130)).]

[C̄ with morpholine in dry ether ppts. morpholine HCl and yields (131) ω-(morpholino)-acetophenone (*N*-(phenacyl)morpholine), m.p. 50–52° (132) (corresp. B̄.HCl, m.p. 222–223° cor. (133), 219–223° (134), 213–214° dec. (131), 212–214° (132); corresp. B̄.PkOH, m.p. 156–157° (132)).]

[C̄ (1 mole) with *N′*-phenylpiperazine (2 moles) in dry ether at room temp. for several hrs. (136) or C̄ (1 mole) with *N′*-phenylpiperazine (1 mole) + slight excess anhydr. Na_2CO_3 in alc. refluxed ½ hr. (136) gives 80–85% yield *N*-phenacyl-*N′*-phenylpiperazine, m.p. 106–108° cor. (136) (corresp. B̄.HCl, m.p. 210–212° cor.; corresp. oxime, m.p. 157–158° cor. (136)).]

[Note, however, that C̄ with 3-carbethoxy-2-methylpyrrole + $AlCl_3$ in CS_2 does not acylate the nitrogen but gives Friedel-Crafts type reaction yielding (137) 3-carbethoxy-2-methyl-5-phenacylpyrrole, m.p. 205°.]

With tertiary aliphatic amines. [Direct addn. of C̄ to Me_3N appears not to have been reported; the quaternary salt to be expected, viz., phenacyl-trimethyl-ammonium chloride, m.p. 204° dec. (138), 202° (121), has been prepd. indirectly.]

With tertiary aromatic amines. [The quaternary salt, viz., dimethyl-phenyl-phenacyl-ammonium chloride, to be expected from C̄ + dimethylaniline is unreported.]

With tertiary heterocyclic amines. (See also below under Ⓓ's.)

[C̄ (1 mole) with pyridine (1+ moles) in dry C_6H_6 on warming gives (25% yield (139)) phenacyl-pyridinium chloride, m.p. 109–110° (139), 113° (140); note that this prod. with aq. 20% NaOH at room temp. [illegible] benzoic acid (1:0715) and (30% yield (141) [illegible] b.p. 127° at 12 mm. (141). — For st[illegible]5.6° (142) or in 90% alc. at 30.5° (16) cf. (112) see indic. refs.]

Behavior of C̄ with Arylhydrazines

(See also below under Ⓓ's.) — C̄ with many arylhydrazines does *not* yield the corresp. arylhydrazones because the reaction takes a different course.

C̄ (2 g.) with phenylhydrazine (1.4 g.) in warm EtOH (20 ml.) contg. $NaOAc.3H_2O$ in aq. (10 ml.) ppts. (14) a yellow solid, m.p. 137° dec. (14), regarded as 1,3-diphenyl-(1,2-diazacyclobutene-2). — Similarly, C̄ with *o*-tolylhydrazine gives (14) 1-(*o*-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 147.2° (14); C̄ with *p*-tolylhydrazine gives (14) 1-(*p*-tolyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 159.8° dec. (14); C̄ with *p*-nitrophenylhydrazine gives (14) 1-(*p*-nitrophenyl)-3-phenyl-(1,2-diazacyclobutene-2), m.p. 173° dec. (14). — [For further discussion of structures of these prods. see also (143).]

Behavior of $\bar{C}$ with Other Miscellaneous Nitrogeneous Reactants

$\bar{C}$ with diazomethane in dry ether + MeOH for 12 hrs. gives (88% yield (144)) 3-chloro-2-phenyl-1.2-epoxypropane (α-chloromethyl-α-phenyl-ethylene oxide), b.p. 135–137° at 17 mm. (144).]

Ⓓ **Chloromethyl phenyl ketoxime:** cryst. from CS_2, m.p. 88 5–89° (4), 88–89° (17). [From $\bar{C}$ (1 mole) + hydroxylamine hydrochloride (3 moles) in dil. MeOH stood overnight, prod. pptd. by addn. of aq. (4); note that this oxime on Beckmann rearr. with PCl_5 gives (4) ω-chloroacetanilide, m.p 134.5° (5)]

Ⓓ **Chloromethyl phenyl ketone 2,4-dinitrophenylhydrazone:** orange cryst., m.p. 212° cor. (145). [See above for behavior of $\bar{C}$ with various other arylhydrazines.]

Ⓓ **Chloromethyl phenyl ketone semicarbazone:** m p. 160° on "Maquenne bloc" (1), 156° (146), 149° (147). [From $\bar{C}$ (3.1 g.) in alc. (25 ml) with semicarbazide hydrochloride (2.2 g.) in aq. (12.5 ml.) at 40° on addn of $NaHCO_3$ (1.7 g.) in small increments; yield 71% (147); for study of chem. behavior of this prod see (147).]

— *N*-(Phenacyl)phthalimide (ω-phthalimidoacetophenone) [Beil. XXI-479]: m.p. 167° u.c. (148), 166° (149). [This prod. has never been reported from C + K phthalimide but has been prepd. indirectly. However, for its prepn. from phenacyl *bromide* with K phthalimide see (150).]

— *N*-(Phenacyl)tetrachlorophthalimide (ω-(tetrachlorophthalimido)acetophenone): pl. from $CHCl_3$ on pouring into MeOH, m p. 258–259° (151). [From $\bar{C}$ (?) or phenacyl bromide with K tetrachlorophthalimide (151)]

Ⓓ **Condensation prod. from $\bar{C}$ with *N*-methyl-β-(carbohydrazido)pyridinium *p*-toluenesulfonate:** cryst. from EtOH/ether 1:1, m.p. 120° cor. (152). [From $\bar{C}$ + the quat. salt of nicotinic acid hydrazide with methyl *p*-toluenesulfonate (152).]

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(11) Conant, Kirner, *J. Am. Chem. Soc.* **46**, 239, 250 (1924). (12) Kohlrausch, Pongratz, *Monatsh.* **64**, 379 (1934). (13) Dijkstra, *Chem Weekblad* **34**, 354–355 (1937). (14) Hoogeveen, *Rec. trav. chim.* **50**, 669–678 (1931). (15) Levin, Hartung, *Org. Syntheses* **24**, 25–28 (1944). (16) [illegible] *J. Am Chem. Soc* **49** 2078– [illegible] neva, [illegible] (20) [illegible]

(21) Sadtler, *Chem. Industries* **40**, 584–586 (1937) (22) Barker, Danner (to Secretary of War, U.S.A.), U.S. 2,146,715, Feb. 14, 1939; *Cent.* **1939**, I 5100, *C.A.* **33**, 3920 (1939). (23) von Frantzius (to Hercules Gas Munitions Corp), U S. 2,068,159, Jan. 19, 1937; *Cent* **1937**, I 3112; *C.A.* **31**, 2010 (1937). (24) Kobe, U.S. 1,993,610, March 5, 1935; *Cent* **1935**, I 3750, *C.A.* **29**, 2631 (1935). [illegible] U.S. 1,864,754, June 28, 1932 [illegible] Cent [illegible] Feb. [illegible] Cent [illegible] C.A [illegible] 643 [illegible] Han [illegible] (35) [illegible] l, Crafts, *Ann chim.* (6) 1, [illegible] 8) Matheson, Humphries, *J. C*[illegible] (4) [illegible] (40) Szper, *Bull soc. chim.*

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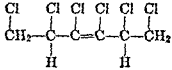
3:1220 1,2,3,4,5,6-HEXACHLOROHEXENE-3 $C_6H_6Cl_6$ **Beil. S.N. 11**



M.P. 58–59° (1) **B.P. 110–112° at 2 mm. (1)**

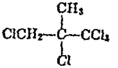
Colorless cryst. from pet ether.

[For prepn from hexadiene-2,5-yne-3 (divinylacetylene) (2) with excess Cl_2 in CCl_4 for 12 hrs. (10% yield (1)) see (1).]

Č fails to react with Cl_2 even at elevated temperatures in light, and is unaffected by hot HNO_3 or by O_3; alk $KMnO_4$ causes complete decomposition (1).

3:1220 (1) Coffman, Carothers, *J. Am. Chem. Soc.* **55**, 2040–2047 (1933). (2) Nieuwland, Calcott, Downing, Carter, *J. Am. Chem. Soc.* **53**, 4200–4202 (1931).

3:1265 1,1,1,2,3-PENTACHLORO-2-METHYLPROPANE $C_4H_5Cl_5$ **Beil. S.N. 10**



M.P. 59.5° (1)

[For prepn. of Č from 1,1,3-trichloro-2-methylpropene-1 (3:5025) with Cl_2 see (1).]

3:1265 (1) Jacob, *Bull. soc. chim.* (5) **7**, 581–586 (1940).

3:1270 CHLORAL HYDRATE $Cl_3C—CH(OH)—OH$ $C_2H_3O_2Cl_3$ Beil. I - 619
I_1-(329)
I_2-(680)

M.P.	**59–60°**	(1) (2)
	57°	(3) (4) (5)
	54°	(6)
	51.6–51.7°	(7)
	51.4°	(8)
	50.8°	(9)
	50.4–50.6°	(10)
	50–51°	(11)
	48.1°	(17)
	47.4°	(6)
	46.5–47.5°	(10)
	46–47°	(12)
	46°	(13)

[See also anhydrous chloral (3:5210) and chloral ethylalcoholate (3:0860).]

The m.p. of C̄ is profoundly affected by mode of heating and by pressure (1) (2) but when taken in test tube in ord. m.p. apparatus is claimed to be consistently 59–60° (2). — [For especially extensive studies on the m.p. of C̄ see (1) (2) (6) (10).]

C̄ undergoes a transition point at 32° detectable by dilatometric methods (15). Furthermore, C̄ on heating dissociates into anhydrous chloral and H_2O; the temperature at which dissocn. begins is unknown, but dissocn. is complete at 78° (15).

Ordinary C̄ is definitely the monohydrate, but other hydrates of chloral (3:5210) have been claimed (6). However, the suggestion (16) that C̄ may exist in two modifications appears to be discredited (6) (10).

[For study of crystal structure of C̄ see (18); for density and refractive index of various solns. of C̄ in aq., EtOH, or toluene see (12); for study of toxicity of C̄ see (19).]

Note that C̄ on htg. does *not* give inflammable vapor (diff. from chloral ethylalcoholate (3:0860).

C̄ is eas. sol. in aq. or alc.; much less sol. in $CHCl_3$ or toluene. [E.g., 1 pt. aq. dissolves following parts C̄ at indic. temps.: at 0°, 2.4; at 5°, 2.9; at 10°, 3.8; at 15°, 4.9; at 20°, 6.6; at 25°, 8.3; at 30°, 10.1; at 35°, 12.1; at 40°, 14.3 pts. C̄ (20).] — Aq. solns. of C̄ are frequently designated as chloral sirup; for study of stability of such solns. see (21).

CHEMICAL BEHAVIOR OF C̄

Important note. The chemistry of chloral hydrate (C̄) on one hand and that of anhydrous chloral (3:5210) on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. Most of the definite chemical reactions of chloral hydrate have been associated with the text of anhydrous chloral (3:5210), which should always be consulted. Certain methods for the detection and for determination of chloral and chloral hydrate, however, are brought together here under the latter.

Determination of C̄

For the quantitative detn. of C̄ several different principles have been employed as further explained below.

By behavior with alkali. This method is based upon the fact that C̄ with aq. alkali undergoes hydrolytic cleavage to $CHCl_3$ (3:5050) and formic acid (1:1005); since the

latter is neutralized 1 equivalent of alkali is used up for each mole of formic acid produced and therefore for each mole of C̄ originally present. Since on the one hand the $CHCl_3$ produced is readily volatile and since on the other it is itself attacked by the excess alkali, some standardization of conditions is required. The process usually involves use of a known amount (excess) of standard alkali followed by back titration with standard acid.

[For especially valuable summaries and discussion of this method see (22) (23); for additional material on characteristics of this method see (24) (25) (26) (27) (28) (29) (30) (31) (32) (33) (34) (35) (41); for discussion of detn. of the formate produced see (22).]

If the sample contains other substances which independently react with alkali and thus interfere with the above method, C̄ may be determined by reduction to acetaldehyde (1:0100) and characterization of the latter. E.g., C̄ with Zn + strong HCl (36) (37), or with Zn + dil. H_2SO_4 (37) (38) (27) cf. (42), gives acetaldehyde (1:0100); this may be detd. as *p*-nitrophenylhydrazone (36) (or otherwise) or if H_2SO_4 was used total chloride ion may be determined (42). This reduction to acetaldehyde is of value in detn. of C̄ in presence of $CHCl_3$ (3:5050) or of α,α,β-trichloro-*n*-butyraldehyde ("butyrchloral") (3:5910) (38).

By determination of total chlorine as chloride ion. In addition to the reduction methods *(mentioned in the preceding paragraph) for conversion of all the chlorine of C̄ to chloride* ion, this may also be effected by complete hydrolysis with alkali (usually alcoholic alkali best in pressure bottle (39)) (40) (41); for extensive review of methods based on this principle see (22); the total chloride ion is afterward detd. by conventional methods.

By oxidation methods. By appropriate reagents C̄ can be oxidized to trichloroacetic acid (3:1150); by use of a known amount (excess) of standard soln. of oxidant followed by back titration to determine residual oxidant, the amount corresp. to oxidn. of C̄ can be detd. For studies of this method using I_2 (22) (42) (34) (43), Br_2 (42), $KMnO_4$ (42), or $(NH_4)_2S_2O_8$ (44) see indic. refs.

Detection of C̄ by Various Color Reactions

With various phenols. [For color tests with resorcinol (1:1530) + aq. alk. (45), with pyrogallol (1:1555) + 66% H_2SO_4 *(use in distinction from "butyrchloral" (3:5910) (46))*, with phloroglucinol (1:1620) + aq. alkali (47) (49) see indic. refs.]

[For behavior of C̄ with resorcinol (1:1530) + KBr + conc. H_2SO_4 see (52).]

With pyridine + aq. alk. Since C̄ with aq. alk. on warming gives $CHCl_3$ (3:5050), detection of the latter by means of the pink to red color produced with pyridine in pres. of conc. aq. alkali (Fujiwara reaction) may be used as indirect test for C̄ (48) (51). Note, however, that the test is not specific since it is given by various other trihalogen compounds. [For further information on the Fujiwara reaction see also under trichloroethylene (3:5170).]

With fuchsin-aldehyde reagent. Note that C̄ (unlike chloral (3:5210)) does *not* give color with fuchsin-aldehyde reagent (50).

Ⓓ **1,1,1-Trichloro-2-methylpropanol-2 ("Chloretone"):** M.p. 96°. Convert C̄ with aq. alk. to $CHCl_3$ (3:5050) and derivatize the latter by combination with acetone to "chloretone" (3:2662).

3:1270 (1) Banchetti, *Ann. chim. applicata* **31**, 422–427 (1941), *Cent.* **1942**, II 1770, *C.A.* **38**, 2313 (1944). (2) Banchetti, *Ann. chim. applicata* **31**, 463–466 (1941), *Cent.* **1942**, II 2577; *C.A.* **38**, 2314 (1944). (3) Ingold, *J. Chem. Soc.* **125**, 1536–1537 (1924). (4) Meyer, Dulk, *Ann.* **171**, 74–76 (1874). (5) Petrikaln, Hochberg, *Z. physik. Chem.* **B-4**, 300 (1929). (6) van Rossem, *Z. physik. Chem.* **62**, 681–712 (1908). (7) Tsakalotos, *Bull. soc. chim.* (4) **13**, 282–283 (1913). (8) Bellucci, *Gazz. chim. ital.* **43**, I 527 (1913). (9) Ramsay, Young, *Phil. Trans.* **177**, I 77 (1886). (10) Wall, *J. Phys. Chem.* **4**, 21–32 (1900).
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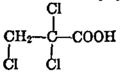
I 3221; *C.A.* **24**, 4586 (1930). (28) Andron, *J. pharm. chim.* [illegible]
I 1845; *C.A.* **23**, 3775 (1929). (29) Andron, *Bull. soc. phar* [illegible]
Cent. **1927**, I 1874; *C.A.* **21**, 2045–2046 (1927). (30) Fleury, Maimy, *J. pharm. chim.* (8) **8**, 537–542 (1928); *Cent.* **1929**, I 2092; *C.A.* **23**, 3775 (1929).
[illegible] **1928**, I 1898; *C.A.* **22**, 1652 (1928).
[illegible] **1928**, I 1986; *C.A.* **23**, 4014 (1929).
[illegible] *C.A.* **2**, 448 (1908). (34) Kolthoff,
[illegible] (35) Garnier, *Bull. sci. pharmacol.* **15**, 77–82 (1908); *Cent.* **1908**, I 1492; *C.A.* **4**, 234 (1910); cf. *Z. anal. Chem.* **49**, 249 (1910). (36) Griebel, Weiss, *Z. Untersuch. Lebensm.* **56**, 163 (1928). (37) Personne, *Ann.* **157**, 113–115 (1871).
(3[illegible] 148; *C.A.* **6**, 1337–1338 (1912).
(3[illegible] (40) Lormand, *J. pharm. chim.*
(8[illegible]
[illegible] *Cent.* **1928**, II 591; not in *C.A.*
[illegible]
(1903); *Cent.* **1904**, I 480–481. (47) Jaworowski, *Z. anal. chem.* **37**, 60–61 (1898). (48) Ross, *J. Biol. Chem.* **58**, 641–642 (1923/24). (49) Kul'berg, Presman, *Farm. Zhur.* **13**, No. 3, 12–14 (1940); *Ce*[illegible]
(51) Ad[illegible]
(8) **22**, 68–[illegible]

3:1275 α,α,β-TRICHLOROPROPIONIC ACID $C_3H_3O_2Cl_3$ Beil. II — II_1— II_2-(228)



M.P. [65–66° (4)]
60° (1)
50–52° (2)

Colorless very hygroscopic cryst.; note that m.p. is rapidly lowered by exposure to moist air (1). — Eas. sol. aq., alc., C_6H_6; best crystd. from CS_2.

[For prepn. of $\bar{C}$ from α,α,β-trichloropropionaldehyde (3:9033) by oxidn. with fumg. HNO_3 (2) (1) or by aq. acid solns. of chlorates + cat. (4) see indic. refs.; from 1,2,2,3-tetrachlorobutene-3 (3:9060) by oxidn. with excess aq. $KMnO_4$ see (3).]

$\bar{C}$ titrates readily as monobasic acid; Neut. Eq., calcd. 177.5; found, 176.6 (2).

[$\bar{C}$ in abs. alc. contg. a little H_2SO_4, refluxed 1 hr. gives (2) ethyl 1,1,2-trichloropropionate, b.p. 121° at 55 mm., $D_4^{25} = 1.36$, $n_D^{25} = 1.458$ (2).]

[For conversion of $\bar{C}$ to acid chloride with $SOCl_2$ or $S_2O_2 + Cl_2$ + cat. see (5).]

3:1275 (1) Muskat, Becker, *J. Am. Chem. Soc.* **52**, 817–818 (1930). (2) Berlande, *Bull. soc. chim.* (4) **37**, 1392 (1925). (3) Berchet, Carothers, *J. Am. Chem. Soc.* **55**, 2008 (1933). (4) Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,370,577, Feb. 27, 1945; *C.A.* **39**, 4085 (1945). (5) Lichty (to Wingfoot Corp.), U.S. 2,361,552, Oct. 31, 1944; *C.A.* **39**, 2297 (1945).

3:1280 α,α,β-TRICHLORO-*n*-BUTYRIC ACID ("Trichlorocrotonic acid")

H Cl
$CH_3.C\,.\,C.COOH$
Cl Cl

$C_4H_5O_2Cl_3$ Beil. II - 280; II_1-(121); II_2-(255)

M.P. 60° (1) B.P. 236-238° (3)
57.9° (2)

Colorless hygroscopic lfts. or ndls. from pet. ether; deliquesces in moist air to yield an oil sol. in 20-25 pts. aq. (4). [New comml. prod. (1942) in U.S.A.]

[For prepn. (100% yield (5)) from α,α,β-trichloro-*n*-butyraldehyde hydrate (*n*-butyrchloral hydrate) (3:1905) via actn. of 2 pts. fumg. HNO_3 (D = 1.504) at 30° (5) (6) or with aq. acid solns. of chlorates + cat (8) see indic. refs.; for prepn. from α-chlorocrotonic acid (3:2760) or α-chloro-isocrotonic acid (3:1615) by addn. of Cl_2 see (1).]

$\bar{C}$ with Zn dust and aq. gives excellent yield (5) of α-chlorocrotonic acid (3:2760), m.p. 99-100° (5).

Na$\bar{A}$ on warming (4) or boilg. (3) with aq. dec. into CO_2 and 1,1-dichloropropene-1 (3:5120), b.p. 78°. — Pb$\bar{A}_2$ (7) or Pb$\bar{A}_2$.2H_2O (3) is insol. cold aq., spar. sol. hot aq., but eas. sol. in alc. or ether.

$\bar{C}$ with PCl_5 (3) yields α,α,β-trichloro-*n*-butyryl chloride, b.p. 162-166° (3).

—— Methyl α,α,β-trichloro-*n*-butyrate: unreported.

—— Ethyl α,α,β-trichloro-*n*-butyrate: b.p. 212° (see 3:6380).

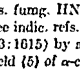
—— α,α,β-Trichloro-*n*-butyramide: scales from alc., m.p. 96° (3). [From α,α,β-trichloro-*n*-butyryl chloride (above) with conc. aq. NH_4OH (3).]

—— α,α,β-Trichloro-*n*-butyranilide: unreported

—— α,α,β-Trichloro-*n*-butyr-α-naphthalide: unreported.

3:1280 (1) Kahlbaum, *Ber.* 12, 2337 (1879). (2) Kendall, *J. Am Chem Soc.* 36, 1231 (1914). (3) Judson, *Ber.* 3, 785-788 (1870) (4) Valentin, *Ber.* 28, 2661-2663 (1895). (5) Roberts, *J. Chem. Soc.* 1938, 779. (6) Krämer, Pinner, *Ber.* 3, 389 (1870). (7) Garzarolli-Thurnlack, *Ann.* 182, 184 (1876). (8) Plump (to Pennsylvania Salt Mfg. Co), *U.S* 2,370,577, Feb. 27, 1945; *C.A.* 39, 4085 (1945).

3:1285 2-CHLORONAPHTHALENE



$C_{10}H_7Cl$ Beil. V - 541; V_1-(262); V_2-(445)

M.P.		B.P.			
61°	(1)	256.5° cor.		(20)	$n_D^{70.7}$ = 1.60787 (12)
60°	(2)	256°		(2)	
59.5-60°	(3)	255.6° cor.	at 752 mm.	(10)	(D_4^{70} = 1.178) (12)
58.0-59.8°	(4)	264-266° cor.	at 751 mm.	(13)	(n_D^{70} = 1.631) (12)
59°	(5)	251-252°		(18)	
58.6°	(6)	121-122°	at 12 mm.	(12)	
58.5°	(7)	119.6-119.8°	at 11 mm.	(4)	
58-59°	(8)				
58°	(9)				
57.4-57.8°	(10)				
56.7°	(11)				
56.5°	(18)				
56°	(12) (13) (14) (21) (27)				
55°	(15)				

[For 1-chloronaphthalene see 3:6875.]

Colorless lfts. from alc.; eas. sol. alc., ether, C_6H_6, $CHCl_3$, CS_2. — *Volatile* with steam.

[For prepn. from β-naphthylamine [Beil. XII-1265, XII_1-(532)] via diazotization and use of Cu_2Cl_2 reaction (yields: 90–95% (17), 82% (15), 75–80% (10)) (3) or even on boilg. diazonium salt soln. with conc. HCl (1) (18), or from diazonium/$ZnCl_2$ cpd. on addn. to phenol at 60° (44% C̄ + 35% hydroxybiphenyl + 13% diphenyl ether (39)), see indic. refs.; from β-naphthol (*1:1540*) with PCl_5 at *135–140°* for 24 hrs. as directed (30% yield (19)) (20) (13) cf. (16) or from *tris*-(β-naphthyl)phosphoric acid dichloride by htg. at 310° (21) or from sodium β-naphtholate with PCl_3 in toluene (55% yield (22)) see indic. refs.; from sodium β-naphthalenesulfonate with PCl_5 via conv. to β-naphthalenesulfonyl chloride and distn. of latter with a second mole of PCl_5 see (13); from mercury *bis*-(β-naphthyl) with $SOCl_2$ see (2); from di-β-naphthyl sulfone with PCl_5 see (23); from 6-chloronaphthoic acid-1 (3:4845) by decarboxylation in quinoline at 225° in pres. of copper chromite cat. see (8); for formn. of C̄ in small proportion from 1-chloronaphthalene (3:6878) by htg. with $AlCl_3$ (9) or from naphthalene dichloride by actn. of alkali (24) see indic. refs.]

[For sepn. of C̄ from 1-chloronaphthalene (3:6878) by fractional freezing of appropriate solutions see (25).]

[For thermal anal. of systems of C̄ with $SbCl_3$ (14) (26) or $SbBr_3$ (14) see indic. refs.; with β-naphthol (1:1540), with β-naphthylamine, or with 2-methylnaphthalene (1:7605) see (5), with PkOH see (11).]

[C̄ with even twice calcd. amt. 5% Na/Hg in alc. for 22 hrs. is *not* reduced but can be recovered almost quant. (27).]

[C̄ with Li in dry ether subsequently treated with Me_2SO_4 gives (43% yield (28)) 2-methylnaphthalene (1:7605). — C̄ with chlorobenzene + Na in xylene refluxed 12 hrs. gives small yield (38) 2-phenylnaphthalene [Beil. V-687], m.p. 101.5° (38).]

[C̄ with strong alc. KOH *in s.t. at 220°* is *unchanged* (13), but C̄ with 5 moles 3–25% aq. NaOH htd. under press. 1 hr. at 350–360° in pres. of Cu gives (29) a mixt. of β-naphthol (1:1540) + α-naphthol (1:1500) cf. (30).]

[C̄ on mononitration as directed (31) gives 2-chloro-8-nitronaphthalene [Beil. V-556], yel. ndls. from alc., m.p. 116° (31) (of the other theoretically possible mononitro C̄ isomers *only the following are known, and these have been prepd. indirectly:* viz., *1-nitro-2-chloro*-naphthalene, m.p. 99–100° (32), 3-nitro-2-chloronaphthalene, m.p. 105° (33), 4-nitro-2-chloronaphthalene, m.p. 79° (34), 5-nitro-2-chloronaphthalene, m.p. 100.5° (37).]

tha-

thor

m.p.

175° (17), and no later work appears to be recorded as to whether these are the same and if so which.]

[C̄ on trinitration, e.g., by soln. in 8 pts. abs. HNO_3 at 0°, or better (38% yield (15)) by addn. of C̄ (2 g.) to a mixt. of abs. HNO_3 (16 ml.) + conc. H_2SO_4 (8 ml.) at 0°, followed by warming as directed, gives 2-chloro-1,6,8-trinitronaphthalene, pale *yel. cryst. from* AcOH, m.p. 193°, white ndls. from C_6H_6, m.p. 194° (15).]

[C̄ on cat. oxidn. with air at 250–300° gives (35) 53% phthalic anhydride (1:0725) + 47% 4-chlorophthalic anhydride (3:2725).]

[For chloromethylation of C̄ with paraformaldehyde + HCl gas in AcOH see (40).]

Ⓓ **2-Chloronaphthalenesulfonamide-8 (7-chloronaphthalenesulfonamide-1)**: cryst. from dil. alc., m.p. 231–232° u.c. (36). [From C̄ with chlorosulfonic acid as directed, followed by conversion of the intermediate 2-chloronaphthalenesulfonyl chloride-8, m.p. 124–126° u.c., with $(NH_4)_2CO_3$ to desired sulfonamide (36).]

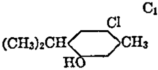
—— **2-Chloronaphthalene picrate**: m.p. 81.5° (by thermal anal. *(11)*).

3:1285 (1) Liebermann, Palm, *Ann.* **183**, 270 (1876). (2) Heumann, Köchlin, *Ber.* **16**, 1627 (1883). (3) Hampson, Weissberger, *J. Chem. Soc.* **1936**, 394. (4) Gockel, *Z. physik. Chem.* **B-29**, 86 (1935). (5) Grimm, Gunther, Titus, *Z. physik. Chem.* **B-14**, 195, 199, 202 (1931). (6) Parts, *Z. physik. Chem.* **B-10**, 265 (1930). (7) L. Klemm, W. Klemm, Schiemann, *Z. physik. Chem.* **A-165**, 384 (1933). (8) Price, Chapin, Goldman, Krebs, Shafer, *J. Am. Chem. Soc.* **63**, [illegible]

[illegible] (1876); *Ber.* **9**, 663–666 (1876). (14) Menschutkin, *J. Russ. Phys.-Chem. Soc.* **44**, 1084 (1912); *Cent.* **1912**, II 1436. (15) van der Kam, *Rec. trav. chim.* **45**, 568–569 (1926). (16) Chattaway, [illegible]). (17) Scheid, *Ber.* **34**, 1813–1815 (1901). (18) Gasior- [illegible] (19) Berger, *Bull. soc. chim.* (3) **35**, 30–32 (1906). (20) [illegible] (2) **25**, 258–259 (1876). [illegible] 3 (1908). (22) Darzens, Berger, *Bull. soc. chim.* (4) **5**, 785–787 (1909). (23) Cleve, *Bull. soc. chim.* (2) **25**, 257 (1876) (24) Armstrong, Wynne, *Chem. News* **61**, 284 (1890); *Ber.* **24**, Referate, 713 (1891) (25) Britton, Reed (to Dow Chem. Co.), U.S. 1,917,822, July 11, 1933; *Cent.* **1933**, II 2194; *C.A.* **27**, 4547 (1933). (26) Vasil'ev, *J. Russ. Phys.-Chem. Soc.* **49**, 428–431 (1917); *Cent.* **1923**, III 668; *C.A.* **18**, 1418 (1924). (27) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 389 (1921/22) (28) Vesely, Stursa, *Collection Czechoslov. Chem. Commun.* **4**, 142 (1932); *Cent.* **1932**, I 3060. (29) Britton, Stearns (to Dow Chem. Co.), U.S. 1,996,745, April 9, 1935; *Cent.* **1935**, II 2126, *C.A.* **29**, 3354 (1935). (30) Hale, Britton (to Dow Chem. Co.), U.S. 1,882,824, 1,882,825, 1,882,826, Oct. 18, 1932, *Cent.* **1933**, I 309, *C.A.* **27**, 731 (1933).

(31) Armstrong, Wynne, *Chem. News* **59**, 225 (1889). (32) Hodgson, Leigh, *J. Chem. Soc.* **1937**, 1352–1353. (33) Hodgson, Elliott, *J. Chem. Soc.* **1934**, 1705–1706. (34) Hodgson, Elliott, *J. Chem. Soc.* **1936**, 1153. (35) Pongratz, Bassi, Fuchs, Suss, Wüstner, Schober, *Angew. Chem.* **54**, 22–26 (1941); *C.A.* **35**, 3248 (1941). (36) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 511–514 (1940). (37) Hodgson, Turner, *J. Chem. Soc.* **1942**, 723–725, *C.A.* **37**, 879 (1943). (38) Chattaway, Lewis, *J. Chem. Soc.* **65**, 871–872 (1894). (39) Hodgson, Foster, *J. Chem. Soc.* **1942**, 582–583. (40) Horn, Warren, *J. Chem. Soc.* **1946**, 144.

3:1293 *p*-CHLOROTHYMOL $C_{10}H_{13}OCl$ Beil. VI - 539
(4-Chloro-2-isopropyl-5-methylphenol) VI_1-(266)
VI_2-(499)



M.P. 62–64° (1) (2) (3)	B.P. 259–263°		(10)
61° (4)	258–259°		(3)
59–60° (5) (6)	143–147° at 18–20 mm.		(4)
59° (7)			
58° (8)			
58–60° (9)			

[*See also p-chlorocarvacrol* (3:0480)]

Note that C̄ is also known as 4-chlorothymol (Beilstein) and as 6-chlorothymol (C.A.) according to differing methods of numbering the thymol nucleus.

PREPARATION OF C̄

From thymol. [For prepn. of C̄ from thymol (1:1430) by chlorination with Cl_2 in aq. Na_2CO_3 (80% yield (10)), with Cl_2 in AcOH (50% yield (8)), or with SO_2Cl_2 (1) (9) in $CHCl_3$ (5) see indic. refs.]

From 4-chloro-3-methylphenol (4-chloro-*m*-cresol). [For prepn. of C̄ from 4-chloro-3-methylphenol (3:1535) by conversion with isopropyl alcohol or isopropyl chloride

(3:7025) (11) or with propylene (3) to 4-chloro-3-methylphenyl isopropyl ether and subsequent rearr. (11) (3), e.g., with H_2SO_4/AcOH (6), to C̄, see indic. refs.]

From other sources. [For prepn. of C̄ from 4-amino-2-isopropyl-5-methylphenol via diazotization and use of $CuCl_2/ZnSO_4$ see (4).]

BIOCHEMICAL ASPECTS AND USES OF C̄

C̄ as a halogenated phenol has been widely considered as an antiseptic, bactericide, disinfectant, germicide, fungicide, etc.; while this aspect cannot here be recorded in detail, the following examples may serve as leading references.

[For general and technical articles on bactericidal (12) (13) (14) (15) (16) (17) (18), fungicidal (12) (19) (20) (21), or anthelmintic (22) action of C̄ see indic. refs.; for patents on various means of improving the aqueous solubility of C̄ for use as germicide see (23) (24) (25) (26) (27) (28) (2) (29); for patent on use of C̄ in mouthwash see (30); for use as disinfectant of a mixt. of C̄ (2 pt.) with camphor (1 pt.) (which mixt. is *liquid* above 5°) see (31).]

CHEMICAL BEHAVIOR OF C̄

Reduction. [C̄ in aq. alk. with H_2 + cat. at 180° and 30 atm. (32), or C̄ in aq. alk. with Fe filings at 170° or at 200° under pressure (33) gives (100% yield (32)) thymol (1:1430), *m.p. 51.5°.*]

Oxidation. C̄ on oxidation with CrO_3 (8) or with MnO_2 in ice-cold conc. H_2SO_4 (1) gives thymoquinone (1:9003), m.p. 45.5°.

Reactions Involving Nuclear Substitution of C̄

Bromination. [C̄ with Br_2 in AcOH gives (8) a mixt. of products.]

Nitration. [C̄ in lt. pet. floated on an aqueous soln. of nitrous acid (from $NaNO_2$ + HCl) for a week gave (8) 4-chloro-2-isopropyl-5-methyl-6-nitrophenol [Beil. VI-542, VI_1-(267)], pale yel. ndls. from alc., m.p. 116° (8) (34). — Note that attempts to effect direct nitration of C̄ with HNO_3 in AcOH below 20° (8) give a mixt. of products; also that C̄ in dry $CHCl_3$ at − 20° with NO_2 (from htg. dry $Pb(NO_3)_2$) gives (8) 4-chloro-3,4,6-trinitro-2-isopropyl-5 methyl-cyclohexadien-2,5-one-1 [Beil. VII_1-(100)], yel. cryst., m.p. about 105° dec. (8).]

Mercuration. [*For patents on mercuration of C̄ see (35) (36).*]

Miscellaneous nuclear substitutions. [Note that NaĀ with benzyl chloride (3:8535) in toluene at 110° for 4 hrs. gives (by nuclear benzylation) (37) 4-chloro-6-benzyl-2-isopropyl-3-methylphenol, b.p. 180° at 3 mm. (37).]

[C̄ with SCl_2 in CS_2 gives (65% yield (5)) a sulfide, $C_{20}H_{24}O_2Cl_2S$, m.p. 110–111°, of undetermined structure.]

Reactions Involving the Phenolic Group of C̄

(See also below under Ⓓ's.)

[C̄ with PCl_5 at 180–200° for 2 hrs. gives (9) 2,5-dichloro-p-cymene [Beil. V-423, V_1-(326)], b.p. 240–243°; this prod. on oxidn. with dil. HNO_3 (D = 1.15) in s.t. at 180° for 10 hrs. gives (38) 2,5-dichloroterephthalic acid [Beil. IX-847], m.p. 305° (38) (corresp. *dimethyl ester, m.p. 136° (38)).*]

[For behavior of C̄ with $POCl_3$ giving compds. of types $ROPOCl_2$ and $(RO)_2POCl$ (R = p-chlorothymyl) see (39); for clinical tests of sodium salt of p-chlorothymylphosphoric acid " thymophogen ") with tuberculosis see (40); for prepn. of such salt see (41).]

—— *p*-Chlorothymyl methyl ether: oil, b.p. 251° cor. at 760 mm. (1). [From C̄ with MeI + KOH (1) or from thymyl methyl ether with SO_2Cl_2 (42).]

—— *p*-Chlorothymyl ethyl ether: unreported.

—— *p*-Chlorothymyl acetate: oil, b p. 112–114° at 2 mm. (43). [From C̄ with Ac_2O (9) or AcCl (44); for Fries rearr. to the corresp. acetophenone deriv. see (44) cf. (43).]

Ⓓ *p*-Chlorothymyl benzoate: m.p. 71–73° (9). [From C̄ with BzCl in aq. KOH (9).]

Ⓓ *p*-Chlorothymyl benzyl ether: m.p. 55° (7).

Ⓓ *p*-Chlorothymyl *o*-nitrobenzyl ether: m.p. 117° (7).

—— *p*-Chlorothymyl *p*-nitrobenzyl ether: unreported.

—— *p*-Chlorothymoxyacetic acid: unreported.

3:1293 (1) Peratoner, Condorelli, *Gazz. chim. ital* 28, I 214–215 (1898). (2) Raschig, Ger. 579,897, July 4, 1933; *Cent.* **1933**, II 1553, *C.A.* **28**, 1142 (1934): U S. 1,816,297, July 28, 1931; *Cent.* **1931**, II 3638; [*C.A.* **25**, 5514 (1931). (3) Schöllkopf (to Rheinisches Kampfer Fabrik) U.S. 2,115,884, May 3, 1938, *Cent.* **1938**, II 2180, *C A.* **32**, 4606 (1938) Brit. 319,205, Aug 8, 1929, *Cent.* **1930**, I 736; *C.A.* **24**, 2468 Ger. 638,756, Nov 21, 1936, not in *Cent.; C.A.* **31**, 3064 (1937): French 681,049, May 8, 1930; *Cent.* **1930**, II 1132, *C A* **24**, 4051 (1930). (4) Skraup, Steinruck (to Rheinische Kampfer Fabrik) Ger. 431,513, July 10, 1926, *Cent* **1926**, II 1462; not in *C.A.* (5) Lesser, Gad, *Ber.* **56**, 977 (1923). (6) Niederl, Natelson, *J. Am. Chem. Soc.* **54**, 1068–1069 (1932). (7) Jones, *J. Chem. Soc.* **1941**, 364. (8) Robertson, Briscoe, *J. Chem. Soc.* **101**, 1968–1971 (1912). (9) Bocchi, *Gazz. chim. ital.* **26**, II 403–406 (1896). (10) Tischenko, *J. Russ Phys.-Chem. Soc.* **60**, 153–162 [illegible]

(11) Raschig, U.S. 1,769,648, July [illegible] 30): Brit. 270,283, June 22, 1928; *Cent.* **1929**, I [illegible] 30, 1932; *Cent.* **1932**, II 1693; *C.A.* **26**, 5972 (19[illegible] *C.A.* **26**, 157 (1932 [illegible] Aug. 16, [illegible] 66–67 (19[illegible] [illegible] 1956 (1932). (19) Eastwood, *Science* **100**, 10–11 (1944). (20) Woodward, Kingery, Williams, *J. Lab. Clin. Med.* **20**, 950–953 (1935); *Cent.* **1936**, I 93, *C.A.* **29**, 5925 (1935)

(21) Woodward, Kingery, Williams, *J. Lab. Clin. Med.* **19**, 1216–1223 (1934), *Cent.* **1935**, I 256; *C.A.* **28**, 6849 (1934). (22) Oelkers, Rathje, *Arch. exptl Path. Pharmakol.* **198**, 317–337 (1941); *Trop. Diseases Bull.* **39**, 767–768 (1942), *C.A* **37**, 1507 (1943). (23) Hueter, Engelbrecht (to Unichem), U.S. 2,267,101, Dec. 23, 1941; *C A.* **36**, 2376 (1942) (24) Schering, A.G., French 870,574, March 16, 1942; *Cent.* **1942**, II 1374; not in *C.A.* (25) Deutsche Hydrierwerke, A G, French 823,289, Jan. 18, 1938; *Cent.* **1938**, I 2587, *C A.* **32**, 5582 (1938) (26) Gelinsky, Ger. 649,126, Aug. 16, 1937; *Cent.* **1937**, II 3627; *C.A.* **31**, 8838 (1937) (27) Goedrich, U.S. 2,073,057, March 9, 1937; *Cent.* **1937**, I 4830; *C.A.* **31**, 3214 (1937) (28) Goedrich (to Goedrich Chem. Co) U.S. 1,930,474, Nov. 17, 1935; *Cent.* **1934**, I 2314, *C A* **28**, 263 (1934). (29) Raschig, Ger. 580,880, July 17, 1933; *Cent.* **1933**, II 2294; *C A.* **28**, 1142 (1934). (30) Pepsodent Co., French 693,083, Nov. 14, 1930; *Cent.* **1931**, I 1481; *C.A.* **25**, 1640 (1931).

(31) Raschig, Ger. 433,293, Aug 23, 1926; *Cent.* **1926**, II 2205, not in *C A.* (32) Schöllkopf (to Rheinisches Kampfer Fabrik), Ger. 432,802, Aug. 11, 1926; *Cent* **1926**, II 1693; not in *C.A.* (33) Raschig, Ger. 396,454, June 6, 1924; *Cent.* **1924**, II 1275; not in *C.A.* (34) Kehrmann, Schön, *Ann* **310**, 106–107 (1900). (35) Christiansen (to Squibb and Sons), U.S 2,252,705, Aug 19, 1941; *C.A.* **35**, 7657 (1941). (36) Christiansen, Moness (to Squibb and Sons), U.S. 2,137,236, Nov. 22, 1938; *C.A.* **33**, 1886 (1939) (37) Klarmann, Gates (to Lehn, Fink, Inc.), U.S 1,926,874, Sept. 12, 1933; *Cent.* **1934**, I 83; [*C A.* **27**, 5896 (1933)]. (38) Wheeler, Giles, *J. Am. Chem. Soc.* **44**, 2611 (1922). (39) Rosenmund, Vogt, *Arch Pharm* **281**, 317–327 (1943); *C.A.* **38**, 5804–5805 (1944). (40) Hisasi, *Beitr. Klin. Tuberk* **92**, 52–57 (1938); *C.A.* **33**, 6794 (1939).

(41) Ayukawa, Japanese 93,182, Oct. 9, 1931; *C.A.* **27**, 1452 (1933). (42) Peratoner, Ortoleva, *Gazz chim. ital.* **28**, I 228 (1898). (43) Klarmann, Shternov, Gates, *J. Am Chem. Soc.* **55**, 2576–2587 (1933). (44) Klarmann, Gates (to Lehn, Fink, Inc), U.S. 1,938,912, Dec. 12, 1935; *Cent.* **1934**, I 2006; *C.A.* **28**, 1472 (1934): Brit. 432,955, Sept. 5, 1935; *Cent.* **1936**, I 809–810, [*C.A.* **30**, 575 (1936)].

3:1300 β-CHLOROISOCROTONIC ACID (*cis*-3-Chlorobuten-2-oic acid-1) $C_4H_5O_2Cl$ Beil. II - 416, II_1-(190), II_2-(396)

```
CH3—C—Cl
    ‖
HOOC—C—H
```

M.P. 62°	(1)	B.P. 194.8° cor. (11)	$D_4^{66.0} = 1.1995$ (7)
61.5°	(2)		$n_D^{66.0} = 1.47039$ (7)
61°	(3) (4) (5) (6) (7) (8)		
60.5°	(9)		
59.5–60.5°	(10)		
59.5°	(11) (17)		

[*See also β-chlorocrotonic acid* (3:2625).]

Cryst. from aq. or pet. ether. — C̄ is somewhat less sol. in aq. than its stereoisomer (3:2625); e g., C̄ is sol. in 52.4 pts. aq. at 19° (12), in 79 pts. aq. at 7° (11). — C̄ is very easily volatile with steam (11) (dif. from β-chlorocrotonic acid (3:2625). — C̄ in either *cis*-α,β-dichloroethylene (3:5042) or *trans*-α,β-dichloroethylene (3:5028) is very much more sol. than the stereoisomeric β-chlorocrotonic acid (3:2625) (13). — C̄ sublimes even at room temp. (11).

For f.p./compn. data and diagram of system C̄ + the stereoisomeric β-chlorocrotonic acid (3:2625) (eutectic, m.p. 38.9° contg. 66.8 mole % C̄) see (14).

Preparation. [The most frequently used method of prepn. of C̄ is that from ethyl acetoacetate (1:1710) with PCl_5; this treatment leads to the formn. of a mixt. of the acid chlorides of C̄ and the stereoisomeric β-chlorocrotonic acid (3:2625) which upon hydrolysis with aq. gives a mixt. of the two acids; from this mixture C̄ is removed (together with any unreacted ethyl acetoacetate) by distillation with steam; the yield of mixed acids is variously reported, e.g., 43.7% (3), 36.5% (9); the yield of C̄ is relatively small, e.g., 26.8% (3), 13% (1). — The PCl_5 reactn. has often been carried out in dry C_6H_6 (8) (15) (9) (3), but its use is regarded (1) as disadvantageous. — For many important details of procedure see indic. refs.]

[For formn. of C̄ from α,β,β-trichloro-*n*-butyric acid (3:0925) by removal of the α- and one β-chlorine atom with Zn see (16); from the stereoisomeric β-chlorocrotonic acid (3:2625) by htg. at 150–160° for 20 hrs. (17) or at 130° in s.t. (18) see indic. refs.]

Chemical behavior. [C̄ in alc. or in aq. NaOH with H_2 + Pd/$BaSO_4$ (4), or C̄ (as NaĀ) with 2½% Na/Hg in aq. (19), yields mainly isocrotonic acid (1:1045) together with some crotonic acid (1:0425) and tetrolic acid, $CH_3—C{\equiv}C—COOH$; note that C̄ is thus dehalogenated more rapidly (4) than the stereoisomeric β-chlorocrotonic acid (3:2625), and that with excess H_2 the products are further reduced to *n*-butyric acid (1:1035).]

C̄ on oxidn. with aq. $KMnO_4$ yields (20) only AcOH (1:1010) and oxalic acid (1:0445).

C̄ with Cl_2 in CS_2 soln. adds 1 mole halogen yielding (16) α,β,β-trichloro-*n*-butyric acid (3:0925), m.p. 52°; C̄ undoubtedly adds 1 Br_2 to yield β-chloro-α,β-dibromo-*n*-butyric acid but the latter has never been reported.

C̄ behaves as a monobasic acid; dissociation const. at 25° = 9.47×10^{-5} (21). — C̄ on neutralization with cold dil. alk. gives Neut. Eq. 120.5. — Note, however, that with strong aq. KOH C̄ is somewhat more resistant than its stereoisomer (3:2625); e.g., C̄ with 3-4 *N* KOH at 115–120° (16) cf. (22) gives acetone (1:5400) + K_2CO_3 + KCl; with 7–8% KOH at 125–130° same + some tetrolic acid.

Salts. [$NH_4H\bar{A}.H_2O$ (11): $Na\bar{A}.½H_2O$, very sol. aq. or alc. (11): $K\bar{A}.H_2O$, sol. in 13.2 pts. alc. at 14° (24): AgĀ, alm. insol. cold aq.; on htg. with aq. in s.t. at 170° dec. much more readily (24) than its stereoisomer (3:2625) into CO_2 + propadiene (allylene):

$Mg\bar{A}_2.5H_2O$, $Ca\bar{A}_2.3H_2O$, $Ba\bar{A}_2.2H_2O$, $Zn\bar{A}_2.2\frac{1}{2}H_2O$, $Mn\bar{A}_2.2H_2O$, $Co\bar{A}_2.6H_2O$, $Ni\bar{A}_2.6H_2O$, all sol. aq. (11): $Pb\bar{A}_2.4H_2O$, spar. sol. aq. (11).]

$\bar{C}$ with PCl_5 (25) or with $SOCl_2$ (26) gives (yield 90% (26)) (29) β-chloroisocrotonyl chloride, b.p. 135–136° at 760 mm.; see also comments under β-chlorocrotonic acid (3:2625).

[$\bar{C}$ (as $K\bar{A}$) with alc. NaOEt on htg. gives after acidification (17) β-ethoxycrotonic acid [Beil. III-371, III_1-(135)], m.p. 137–138° (17), 141° (27); note that during reactn. isomerization has occurred and that this prod. is the same as is similarly obtd. from β-chlorocrotonic acid (3:2625). — $\bar{C}$ (as $Na\bar{A}$) with Na benzylate on htg gives after acidification (28) β-benzyloxycrotonic acid, m.p. 121–122° (28), the same as does the stereoisomer. — $\bar{C}$ (as $Na\bar{A}$) with Na salt of benzyl mercaptan in alc. on htg. gives after acidification (28) β-benzylmercaptoisocrotonic acid, m.p. 130°; note that here isomerization does not occur.]

[For behavior of $\bar{C}$ (as $NH_4\bar{A}$) with $(NH_4)_2SO_3$ yielding β-sulfocrotonic acid (3), or of $\bar{C}$ (as $K\bar{A}$) with K_2AsO_3 yielding (10) β-arsonocrotonic acid, see indic. refs.; note that in both cases the products are identical with those obtd. by similar treatment of β-chlorocrotonic acid (3:2625).]

—— Methyl β-chloroisocrotonate: b.p. 142°. See 3:8028. [For rate of esterification of $\bar{C}$ with MeOH see (30).]

—— Ethyl β-chloroisocrotonate: b.p. 165°. See 3:8325.

Ⓓ *β-Chloroisocrotonamide: lfts. from aq., m p. 109–110° (25).* [From β-chloroisocrotonyl chloride (see above) with conc. aq. NH_4OH (25).] [For study of solubility in *cis*-1,2-dichloroethylene (3:5042) and in *trans*-1,2-dichloroethylene (3:5028) see (13).]

Ⓓ β-Chloroisocrotonanilide: ndls. from alc., m.p. 106° (25) [From β-chloroisocrotonyl chloride (see above) with aniline + excess cold dil. aq. NaOH in 100% yield (25).]

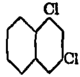
Ⓓ β-Chloroisocroton-α-naphthalide: ndls. from alc., m.p 155° (25). [From β-chloroisocrotonyl chloride (see above) with α-naphthylamine + excess cold dil. aq. NaOH in 100% yield (25).]

3:1300 (1) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **60**, 211–212 (1932): *Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse*, Abt. II-a, **140**, 359–360 (1931). (2) Stelling, *Z. physik. Chem.* **B-24**, 423 (1934). (3) Backer, Beute, *Rec. trav. chim.* **54**, 552–553, 559–560 (1933). (4) Paal, Schiedewitz, Rauscher, *Ber.* **64**, 1521–1530 (1931). (5) Bruylants, Castille, *Bull. soc. chim. Belg.* **34**, 277 (1925). (6) von Auwers, Wissebach, *Ber* **56**, 724 (1923). (7) von Auwers, *Ber.* **45**, 2807 (1912). (8) Michael, Schulthess, *J. prakt Chem.* (2) **46**, 236–237 (1892). (9) Skau, Saxton, *J. Am. Chem. Soc.* **50**, 2693–2701 (1928). (10) Backer, van Oosten, *Rec. trav. chim.* **59**, 50 (1940).

(11) Geuther, Fröhch, *Zeit Chem.* **1869**, 270–271. (12) Michael, Brown, *Am. Chem. J.* **9**, 284 (1887). (13) Lebrun, *Bull. soc chim.* **39**, 429–430 (1930). (14) Skau, Saxton, *J. phys. Chem.* **37**, 183–186 (1933). (15) Scheibler, Voss, *Ber.* **53**, 381–382 (1920) (16) Szenic, Taggesell, *Ber.* **28**, 2665–2667 (1895). (17) Friederich, *Ann.* **219**, 327–346, 363 (1883). (18) Michael, Schulthess, *J. prakt Chem.* (2) **46**, 264–266 (1892). (19) Michael, Schulthess, *J prakt. Chem.* (2) **46**, 250–251 (1892). (20) Kondakow, *J Russ. Phys -Chem Soc.* **24**, 511 (1892).

(21) Ostwald, *Z. physik. Chem.* **3**, 245 (1889). (22) Michael, *J. prakt. Chem.* (2) **38**, 9–10 (1888). (23) Michael, Schulthess, *J prakt Chem.* (2) **46**, 254–255 (1892). (24) Michael, Clark, *J. prakt. Chem.* (2) **52**, 326–329 (1895). (25) Autenrieth, *Ber* **29**, 1665–1670 (1896). (26) Scheibler, Topouzada, Schulze, *J prakt Chem* (2) **124**, 16 (1930). (27) Nef, *Ann.* **276**, 234 (1893). (28) Autenrieth, *Ber.* **29**, 1646–1648 (1896) (29) Scheibler, Voss, *Ber.* **53**, 382 (1920). (30) Sudborough, Roberts, *J. Chem. Soc.* **87**, 1846 (1905).

(31) Michael, Oechslin, *Ber.* **42**, 322 (1909).

3:1310 1,3-DICHLORONAPHTHALENE  $C_{10}H_6Cl_2$ Beil. V - 542
V_1-(262)
V_2-(445)

M.P. 61.5-62° (1) B.P. 291° cor. at 775 mm. (4)
61.5° (2)
61° (3) (6) (12)

Colorless ndls. from alc. — Volatile with steam (4).

[For prepn. of C̄ from 1-amino-2,4-dichloronaphthalene via diazotization and subsequent warming with alc. see (4) (5) (6) (1); similarly from 1-amino-5,7-dichloronaphthalene see (7); from 4-nitronaphthalene-sulfonyl chloride-2 by htg. with excess PCl_5 see (3) (8); from *naphthalene-1,3-bis-(sulfonyl chloride) by distn. with* PCl_5 *see (2); from naphthalene*-tetrachloride-1,2,3,4 (3:4750) with alc. KOH see (9) (10) (4) (11).]

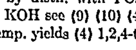
[C̄ in $CHCl_3$, satd. with Cl_2 at ord. temp. yields (4) 1,2,4-trichloronaphthalene (3:2490), m.p. 92° (4).]

[C̄ on nitration yields (4) a mixt. of two dinitro cpds., m.p. 150° and 158° respectively.]

[C̄ in CS_2 treated with $ClSO_3H$ (12) yields a mixt. of 1,3-dichloronaphthalenesulfonic acid-5 [Beil. XI-163] (corresp. sulfonyl chloride, m.p. 148.5°, corresp. sulfonamide, m.p. 272° (12)) and 1,3-dichloronaphthalenesulfonic acid-7 [Beil. XI-183] (corresp. sulfonyl chloride, m.p. 121°, corresp. sulfonamide, m.p. 228° (12)).]

C̄ on oxidn. with CrO_3 in AcOH yields (4) phthalic acid (1:0820) + 2-chloronaphthoquinone-1,4 (3:3580), m.p. 115° (4). — C̄ on oxidn. in s.t. with conc. HNO_3 yields (5) phthalic acid (1:0820).

3:1310 (1) Weissberger, Sängewald, Hampson, *Trans. Faraday Soc.* **30**, 890 (1934). (2) Armstrong, Wynne, *Chem. News* **61**, 93 (1890). (3) Cleve, *Ber.* **19**, 2181 (1886). (4) Cleve, *Ber.* **23**, 954-955 (1890). (5) Cleve, *Ber.* **20**, 449 (1887). (6) Erdmann, *Ann.* **275**, 260-261 (1893). (7) Erdmann, *Ber.* **21**, 3445 (1888). (8) Cleve, *Ber.* **21**, 3274 (1888). (9) Faust, Saame, *Ann.* **160**, 69 (1871). (10) Widman, *Ber.* **15**, 2161-2162 (1882).
(11) Armstrong, Wynne, *Chem. News* **58**, 264-265 (1888). (12) Armstrong, Wynne, *Chem. News* **61**, 274, 284 (1890).

3:1325 2,2'-DICHLOROBIPHENYL  $C_{12}H_8Cl_2$ Beil. V —
V_1-(272)
V_2-(483)

M.P. 61-62° (11)
60.7-62 (1)
60.5-61° (2)
60.5° (3)
60° (4)
59.0-60.5° (5)
59° (6) (7) (8)
58-59° (10)

Pr. from pet. eth. or MeOH.

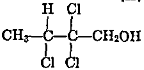
[For prepn. of C̄ from *o*-chloroiodobenzene [Beil. V-220, V_1-(119)] by htg. with Cu powder under various conditions (yield: 40% (1), 20% (11), 10% (2)) see indic. refs.; from 2,2'-dinitrobiphenyl [Beil. V-583, V_1-(273)] with $SOCl_2$ in s.t. at 200-210° for 10 hrs. see (7); from 2,2'-diaminobiphenyl [Beil. XIII-210, $XIII_1$-(57)] via tetrazotization and reaction with Cu_2Cl_2 (6) or by decomp. of $HgCl_2$ complex (80% yield (3)) see indic. refs.; for dis-

cussion of formn. from chlorobenzene (3:7903) during prepn. of phenol by alk. fusion see (12).]

$\bar{C}$ on dinitration with mixt. of conc. HNO_3 and conc. H_2SO_4 as directed (13) (9) gives (41% yield (13)) 2,2′-dichloro-5,5′-dinitrobiphenyl, cryst. from acetone, m.p. 203–204° (13), 205° (9) (a small amt. of an isomer, m.p. 128–129°, is also formed (13)); $\bar{C}$ on tetranitration by htg. with mixt. of 5 pts. fumg HNO_3 ($D = 1.6$) + 20 pts. conc. H_2SO_4 at 100° for 2 hrs. (13) (4) gives (38% yield (13)) 2,2′-dichloro-3,5,3′,5′-tetranitrobiphenyl, cryst from dioxane, m.p. 307–308° (13) (this prod. after melting is converted to higher-melting form, m.p. 316°, recrystn. of which from alc. restores the lower-melting variety (9)).

3:1325 (1) Hampson, Weissberger, *J. Am. Chem Soc* **58**, 2117 (1936). (2) Weissberger, Sängewald, *Z. physik. Chem.* **B-20**, 155 (1933). (3) Schwechten, *Ber* **65**, 1607 (1932). (4) van Alphen, *Rec. trav. chim.* **51**, 454–455 (1932) (5) Williamson, Rodebush, *J. Am. Chem Soc.* **63**, 3019 (1941). (6) Dobbie, Fox, Gauge, *J. Chem. Soc* **99**, 1619 (1911). (7) Mascarelli, Gatti, *Gazz. chim. ital.* **59**, 868 (1929) (8) Mascarelli, Gatti, *Gazz. chim. ital* **63**, 664 (1933). (9) Mascarelli, Gatti, *Gazz. chim ital.* **63**, 658 (1933). (10) Brüll, *Gazz. chim. ital* **65**, 24 (1935).
(11) Bretscher, *Helv. Phys. Acta* **2**, 266–267 (1929). (12) Hale, Britton, *Ind. Eng. Chem.* **20**, 122 (1923). (13) Case, Schock, *J. Am. Chem. Soc.* **65**, 2086–2087 (1943).

3:1336 *d,l*-2,2,3-TRICHLOROBUTANOL-1 $C_4H_7OCl_3$ **Beil. I - 369**
I_1—
I_2-(398)



M.P.	**62°**	(1) (3) (6)	**B.P. 199–200°**	(4)
	61.5–62°	(2)	**120° at 45 mm.**	(2)
	[**57°**	(8)]		

Cryst. from pet. ether. — Insol. cold aq.; spar. sol. hot aq.; eas. sol. alc., ether. — In small quantities can (with caution) be sublimed (2).

[For prepn. of $\bar{C}$ from α,α,β-trichloro-*n*-butyraldehyde (butyrchloral) (3:5910) with fused $Al(OEt)_3$ in boilg. abs. alc. under H_2 or N_2 for 14 hrs. (92% yield (1)), or with fused $Al(OEt)_3$ + $AlCl_3$ in boilg. abs. alc. under H_2 or N_2 for 14 hrs. (3), or with C_2H_5OMgBr in dry ether followed by aq. (5), or by treatment with diethylzinc (60–70% yield (8)) (2), di-*n*-propylzinc (6), or di-isobutylzinc (6) followed by aq. see indic. refs ; for formn. of $\bar{C}$ from urobutyrchloralic acid (see below) by hydrolysis see (4).] [Note that dextrorotatory $\bar{C}$, m.p. 62°, is obtd. (7) from butyrchloral hydrate (3:1905) by action of fermenting yeast.]

[$\bar{C}$ with Zn + very dil. HCl gives (2) 2-chlorobuten-2-ol-1 (3:8240), b.p. 158°. — $\bar{C}$ reduces Fehling soln. on warming]

$\bar{C}$ on oxidn. with conc. HNO_3 gives α,α,β-trichloro-*n*-butyric acid (3:1280).

$\bar{C}$ with PCl_5 on htg. gives (30–40% yield (8)) (2) 1,2,2,3-tetrachlorobutane (3:9078) (volatile with steam) accompanied by much (non-volatile) *tris*-(2,2,3-trichloro-*n*-butyl)-phosphate, colorless ndls. from alc., m.p. 85.3–85.4° (8).

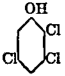
[$\bar{C}$ is sol. in conc. H_2SO_4 on slight warming but readily decomposes if htg. is excessive (2). $\bar{C}$ does not react with PCl_3, or with fumg HBr even at 110° (2).]

$\bar{C}$ on administration to dogs is excreted in the urine as urobutyrochloralic acid [Beil. I-664] (4).

—— **2,2,3-Trichloro-*n*-butyl acetate:** b.p. 217.5° at 730 mm., 131–132° at 70 mm. (2). [From $\bar{C}$ with AcCl in s t. at 110° for several hrs. (2).]

3:1336 (1) Meerwein, Schmidt, *Ann.* **444**, 233–234 (1925). (2) Garzarolli-Thurnlackh, *Ann.* **213**, 369–379 (1882). (3) Meerwein (to F. Bayer and Co.), U.S. 1,572,742, Feb. 9, 1926; *Cent.* **1926**, I 3627; Brit. [illegible]
496 (1882).
Papper, *Ann.*
I 2301; *C.A.* [illegible]

3:1340 2,3,5-TRICHLOROPHENOL



$C_6H_3OCl_3$ Beil. VI —
VI_1—
VI_2-(180)

M.P. 62° (1) (2) (3)

C̄ when dislvd. in hot solvents and cooled gives gels; e.g., a very dil. hot aq. soln. set on cooling to an almost solid translucent gel, partly fibrous and partly crystalline (1). When a soln. of K_2CrO_4 is poured on such a gel contg. $AgNO_3$, distinct but not well-defined Liesegang rings are produced in the gel (1) cf. (4).

C̄ is volatile with steam. — Ionization const. at 23° is 5.0×10^{-8} (3); C̄ can be titrated with $N/10$ alk. using phenolphthalein; Neut. Eq. 197.5 (2).

[For prepn. from 2,3,5-trichloroaniline via diazo reaction see (1) (70% yield) or (2) (57% yield).]

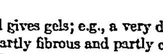
C̄ (1.5 g.) dislvd. in 20% aq. NaOH (20 ml.) and shaken with $(CH_3)_2SO_4$ (5 g.) ppts. (1) methyl ether (1.5 g. = 94% yield), 2,3,5-trichloroanisole, ndls. from alc., m.p. 84° (1), cryst. from acetone, m.p. 82° (4).

Ⓓ 2,3,5-Trichlorophenyl benzoate: from C̄ + BzCl + aq. NaOH, ndls. from alc., m.p. 101° (4), from lgr., m.p. 103° (4).

3:1340 (1) Hodgson, Kershaw, *J. Chem. Soc.* **1929**, 2919–2921. (2) Tiessens, *Rec. trav. chim.* **50**, 114 (1931). (3) Tiessens, *Rec. trav. chim.* **48**, 1066–1068 (1929). (4) Holleman, *Rec. trav. chim.* **39**, 739–740 (1920).

3:1355 2,4-DIMETHYLPHENACYL CHLORIDE
(ω-Chloro-2,4-dimethylacetophenone)

$C_{10}H_{11}OCl$ Beil. VII - 324
VII_1-(172)



M.P. 62°

Long wh. lfts. (from alc.). [For prepn. from *m*-xylene, chloroacetyl chloride (3:5235) + $AlCl_3$ see (1) (3).]

C̄ on oxidn. with aqueous NaOBr soln. for 3 hrs. (2) yields 2,4-dimethylbenzoic ac. [Beil. IX-531], cryst. from dil. MeOH, m.p. 126°. With a large excess of NaOBr and longer time (20 hrs.) C̄ yields 5-bromo-2,4-dimethylbenzoic acid. [Beil. IX-533], m.p. 180–181° (2).

C̄ on oxidn. with alk. $KMnO_4$ soln. gives (3) 2-methylterephthalic acid [Beil. IX-863], m.p. 325–330°, whose dimethyl ester has m.p. 73–74° (4).

C̄ treated with nicotinic acid hydrazide metho-*p*-toluenesulfonate in alc. gives corresp. hydrazone, cryst. from 1:1 EtOH/ether, m.p. 196° cor. (5).

3:1355 (1) Kunckell, *Ber.* **30**, 579 (1897). (2) Fisher, Grant, *J. Am. Chem. Soc.* **57**, 718–719 (1935). (3) Jörlander, *Ber.* **50**, 1460 (1917). (4) Lacourt, *Bull. soc. chim. Belg.* **39**, 136–138 (1930). (5) Allen, Gates, *J. Org. Chem.* **6**, 596–601 (1941).

—— *cis* β-CHLOROACRYLIC ACID HC—Cl ‖ HC—COOH $C_3H_3O_2Cl$ Beil. II - 400, II_1-(186), II_2—

M.P. 63-64°

See 3:2240 *under trans-β-chloroacrylic acid.*

3:1364 DIETHYL *meso*-α,α′-DICHLOROSUCCINATE $COOC_2H_5$ | H—C—Cl | H—C—Cl | $COOC_2H_5$ $C_8H_{12}O_4Cl_2$ Beil. II - 619, II_1—, II_2-(558)

M.P. 63°	(1)	B.P. 125.5° cor. at 12.5 mm. (1)	D_4^{99} = 1.1490 (1)
61.75-62°	(2)		$n_D^{64.5}$ = 1.4266 (1)
57°	(3)		

Ndls. from dil. alc.; very eas. sol. alc., ether. — Volatile with steam.

[For prepn. of $\bar{C}$ from *meso*-α,α′-dichlorosuccinic acid (3:4930) in EtOH with HCl gas see (2) (1); from diethyl fumarate with HOCl see (3).]

3:1364 (1) Kuhn, Wagner-Jauregg, *Ber.* **61**, 485–486, 504 (1928). (2) Kirchhoff, *Ann.* **280**, 214–215 (1894). (3) Henry, *Bull. acad. roy. Belg* (3) **36**, 31–54 (1898); *Cent.* **1898**, II 663.

3:1370 CHLOROACETIC ACID H_2C—COOH | Cl $C_2H_3O_2Cl$ Beil. II - 194, II_1-(87), II_2-(187)

M.P. α-form		M.P. β-form		M.P. γ-form		B.P.		
63°	(1) (2)	56.68°	(99)	52.5°	(10)	189.35°	at 760 mm.	(27) (90) (92)
	(3) (4) (5) (6)	56.6°	(16)	51°	(25)	189°	at 771 mm.	(28)
62.80°	(7)		(17)	50.65°	(7)	189°		(12)
62.53°	(8)	56.3°	(7)	50.2°	(22)	188.8-189.4°		(29)
62.5-63.2°	(9)		(21) (99)	50.05°	(23)	188.6-189.4°		(30)
62.5°	(36)	56.18°	(22)	50°	(20)	188.5-189.5° cor.		(31)
62.3°	(10)	56.01°	(23)			187.8°	at 755.7 mm.	(32)
	(11)	56°	(2) (25)			186°	at 760 mm.	(33)
62.0-62.5°	(9)	55°	(20)			149°	at 207 mm.	(34)
62°	(12) (13)					145.2°	at 180 mm.	(34)
	(14) (15)					140.5°	at 152 mm.	(34)
61.86°	(99)					139.0°	at 141 mm.	(34)
61.8°	(16) (17)					135°	at 122 mm.	(34)
61.7°	(18) (103)					130.1°	at 101 mm.	(34)
61.65°	(99)					122°	at 71 mm.	(34)
61.5°	(19) (20)					108°	at 36 mm.	(34)
	(21)					102.5°	at 27 mm.	(34)
61.4°	(100)					104–105°	at 20 mm.	(1)
	(102) (104)					101°	at 20 mm.	(36)
61.30°	(22)					93°	at 18 mm.	(34)
61.18°	(23)					94°	at 11 mm.	(35)
61-62°	(24)					85-86°	at 11 mm.	(2)
61°	(19) (25)							
60-61°	(26)							

[*See also dichloroacetic acid* (3:6208) *and trichloroacetic acid* (3:1150).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C̄

Polymorphism of C̄. C̄ is known definitely in the above three α, β, and γ forms and perhaps also in a fourth δ form, m.p. 43.75° (23), although last could not be confirmed (22) cf. (7). — The stable (α) form results from rapid condensation of vapor (23), by crystallization of C̄ from aq. soln. (23), or from rapid cooling of fused C̄ (37), although last method could not be confirmed (25); it is also obtained from the β form by seeding with α (9) or from γ form by spontaneous transformation (20), or from either β or γ forms at −20° (22).

The β form results from cooling fused C̄ especially if melt is first htd. above 67° cf. (9) (23), or from γ form on stirring (23) (20) (37) (22) cf. (25) (7).

The γ form results from fused C̄ on cooling without stirring (23) (20) (37) (25) (7).

[For study of transformation points of α and β forms see (21); for studies of effect of pressure on m p. of C̄ see (38) (39) (25) (8).]

Density and refractive index for fused C̄. [Values for these constants are *not* in good accord, viz., $D_4^{65.4}$ = 1.3978 (40), D_4^{65} = 1.3703 (41); $n_D^{65.4}$ = 1.4301 (40), n_D^{65} = 1.4297 (41). — For D_4^t over range 80°–176° see (36).]

Vapor characteristics. [For study of vapor pressure of C̄ over range 85–180° see (42). — For study of volatility with steam see (43).]

Cryoscopic constant. [Molal f.p. constant for C̄ is 5.2° (for 1000 g. C̄) (44) (37); for studies on use of C̄ as cryoscopic solvent see (44) (45) (46) (47).]

Association of C̄. [For studies on extent of association of C̄ in C_6H_6 soln. at 30° (11), in *p*-chlorotoluene (3:8287) (48), in liquid HF (49), in ether (33), or in water (1–9.7% C̄) (50) see indic. refs]

Heat of combustion. [For studies on heat of combustion of C̄ see (51) (52) (53) (54) cf. (55).]

Exchange reactions. [For study of behavior of C̄ with D_2O see (56); with H_2O^{18} see (57).]

Adsorption of C̄ by various adsorbents. [For studies on adsorption of C̄ from aqueous solns. by various forms of carbon (58) (59) (60) (61) (62) (63) (64), by silica gel (60), by synthetic resins (65), by aniline black (66), by filter paper (67), by hide powder (68), by viscose (69), by $Zr(OH)_2$ (70), or by $Fe(OH)_3$ (71) see indic. refs.]

[For studies on adsorption of C̄ from nonaqueous solvents by wood charcoal (72) or from aqueous alc. by charcoal (73) or by casein (74) see indic. refs.]

Distribution of C̄ between solvents. [For data on distribution of C̄ between *aq. and ether* at 18° (75) or at 25° (76) (77) cf. (81); between *aq. and benzene* at 25° (78) or at an unstated temp. (79); between *aq. and toluene* at 25° (78) (80); between *aq. and isobutyl alcohol* at 25° (80); between *aq. and n-amyl alcohol* at 25° (80); between *aq. and isoamyl alcohol* at 25° (80); between *aq. and di-n-butyl ether* at 25° (5); between *aq. and olive oil* at 25° and 37.5° (82) see indic. refs.]

[For data on distribution of C̄ between *aq. and nitrobenzene* at 25° (80); between *aq. and mixts. of benzene + nitrobenzene* (83); between *aq. and o-nitrotoluene* at 25° (80) (84) see indic. refs.]

[For data on distribution of C̄ between *aq. and $CHCl_3$* (3:5050) at 25° (80) (85) (86); between *aq. and CCl_4* (3:5100) at 25° (80) (87) (85); between *aq. and EtBr* at 25° (80) (77); between *aq. and $CHBr_3$* at 25° (85); between *aq. and MeI* at 25° (80) (87) see indic. refs.]

[For data on distribution of C̄ between *aq. and CS_2* at 25° (85); between *aq. $MgSO_4$ or K_2SO_4 solns. and di-n-butyl ether* at 25° (88) (5); between *acetone and glycerol* at 25° (89) see indic. refs.]

Binary Systems Containing $\bar{C}$

Azeotropic systems. [$\bar{C}$ with *mesitylene* (1:7455) forms a const.-boilg. mixt., b.p. 162° at 760 mm., contg. 17 wt. % $\bar{C}$ (90); $\bar{C}$ with *naphthalene* (1:7200) forms a const.-boilg. mixt., b.p. 187.1° at 760 mm., contg. 78 wt. % $\bar{C}$ (91); $\bar{C}$ with *o-cresol* (1:1400) forms a const.-boilg. mixt., b.p. 187.5° at 760 mm., contg 54 wt. % $\bar{C}$ (91).]

[$\bar{C}$ with 1,1,2,2-*tetrachloroethane* (acetylene tetrachloride) (3:5750) forms a const.-boilg. mixt, b p. 146 25° at 760 mm., contg. 1.8 wt % $\bar{C}$ (91); $\bar{C}$ with *pentachloroethane* (3:5880) forms a const.-boilg. mixt, b.p. 158.65° at 760 mm., contg 9.9 wt. % $\bar{C}$ (91); $\bar{C}$ with *hexachloroethane (3:4835) forms a const.-boilg mixt., b p. 171.2° at 760 mm., contg. 25 wt. %* $\bar{C}$ (27); $\bar{C}$ with 1,2,3-*trichloropropane* (3:5840) forms a const-boilg. mixt., b.p. 154.5° at 760 mm., contg. 10 wt. % (92).]

[$\bar{C}$ with *p-dichlorobenzene* (3:0980) forms a const.-boilg. mixt., b.p. 167.55° at 760 mm., contg. 24 5 wt. % $\bar{C}$ (27); $\bar{C}$ with *benzal (di)chloride* (3:6327) forms a const.-boilg. mixt., b.p. 189.1° at 760 mm, contg. 97 wt. % $\bar{C}$ (93).]

[$\bar{C}$ with *bromobenzene* forms a const.-boilg mixt., b p. 154.3° at 760 mm., contg. 11 wt.% $\bar{C}$ (90); $\bar{C}$ with *p-dibromobenzene* forms a const.-boilg. mixt., b.p. 186 3° at 760 mm, contg. 75 wt. % $\bar{C}$ (93).]

Other Physical Data on Binary Systems Containing $\bar{C}$

$\bar{C}$ + aq. [$\bar{C}$ is very eas. sol. aq. (32); for study of hydration at low temps. see (94); for f p./compn. data see (23). — Data on density of aq $\bar{C}$ is fragmentary but for D^{20}_{20} (40), D^{25}_{25} (95), and D^{35}_{35} (95) for certain concns. see indic. refs. (cf. (96) (97) (98)). — For refractive indices of aq. solns. of $\bar{C}$ see (20) (40) — For study of soly. of aq. in $\bar{C}$ + C_6H_6 see (105).]

$\bar{C}$ + H_2SO_4. [For densities, viscosities, and elec. conductivity at 20°, 40°, and 60° over whole compn. range see (12); for f.p./compn. data over range 46–100% $\bar{C}$ (no compound is formed) see (18).]

$\bar{C}$ + acetic acid. (1:1010) [For f p./compn. data and diag., eutectic m.p. −4.0°, contg. 22 mole % $\bar{C}$, see (99) cf. (100) (103)]

$\bar{C}$ + dichloroacetic acid (3:6208). [For f.p./compn. data (100), eutectic m p. −10.5° contg. 30 7 mole % $\bar{C}$ (101), see indic. refs.]

$\bar{C}$ + trichloroacetic acid (3:1150). [For f.p./compn. data (100), eutectic m p. 17.5° contg. 48.5 mole % $\bar{C}$ (101), see indic. refs.]

$\bar{C}$ + miscellaneous organic compds. of Order 1. [For f.p./compn. data on following systems see indic. refs: $\bar{C}$ + C_6H_6 (1:7400) (103); $\bar{C}$ + *naphthalene* (1:7200) (99) (17) (20); $\bar{C}$ + *phenol* (1:1420) (17) (16) (102); $\bar{C}$ + *o-cresol* (1:1400) (16) (102); $\bar{C}$ + *m-cresol* (1:1730) (16); $\bar{C}$ + *p-cresol* (1:1410) (16); $\bar{C}$ + *α-naphthol* (1:1500) (16); $\bar{C}$ + *β-naphthol* (1:1540) (16); $\bar{C}$ + *thymol* (1:1430) (16); $\bar{C}$ + *guaiacol* (1:1405) (16); $\bar{C}$ + *cetyl alc.* (1:5945) (99); $\bar{C}$ + *meso-erythritol* (1:5825) (14); $\bar{C}$ + *benzoic acid* (1:0715) (100); $\bar{C}$ + *o-toluic acid* (1:0690) (100); $\bar{C}$ + *m-toluic acid* (1:0705) (100); $\bar{C}$ + *p-toluic acid* (1:0795) (100); $\bar{C}$ + *phenylacetic acid* (1:0665) (100); $\bar{C}$ + *cinnamic acid* (1:0735) (100); $\bar{C}$ + *crotonic acid* (1:0425) (100); $\bar{C}$ + *dimethyl oxalate* (1:0415) (103); $\bar{C}$ + *dimethyl succinate* (1:3556) (103); $\bar{C}$ + *methyl cinnamate* (1:2090) (103); $\bar{C}$ + *phenyl salicylate* ("Salol") (1:1415) (99); $\bar{C}$ + *piperonal* (1:0010) (99) (104); $\bar{C}$ + *vanillin* (1:0050) (104); $\bar{C}$ + *acetophenone* (1:5515) (104); $\bar{C}$ + *benzil* (1:9015) (104); $\bar{C}$ + *dibenzalacetone* (1:9021) (104)]

$\bar{C}$ + miscellaneous compounds of Order 2. [For f.p./compn. data on following system see indic. refs.: $\bar{C}$ + *urea* (19); $\bar{C}$ + *ethyl carbamate (urethane)* (19).]

TERNARY SYSTEMS CONTAINING C̄

[For f.p./compn. data and diag. of following systems see indic. refs.: C̄ (α-form) + phenol (1:1420) + naphthalene (1:7200) (17); C̄ (β form) + phenol (1:1420) + naphthalene (1:7200) (17).]

USE OF C̄ IN FOODS AND BEVERAGES

General. [For discussion of use of C̄ as fermentation and oxidn. inhibitor or stabilizer in fruit juices, carbonated beverages, etc. (sometimes as "Esterex" (106)), see (106) (107) (108) (109) (110); for study of persistence of C̄ in such use see (111); for patents on such use see (112); for studies of bactericidal action (113) or fungistatic props. (114) of C̄ see indic. refs.]

Toxicity of C̄. [For studies on toxicity of C̄ see (115) (116).]

Detection and determination of C̄ in foods and beverages. [For studies on detection and detn. of C̄ in commercial preservatives (624), in non-alc. beverages (117) (118) or in wines (119) (120) cf. (117) see indic. refs.: for identification of C̄ as $Ba\bar{A}_2$ (optical and crystallographic props.) see (121) (623).]

PREPARATION OF C̄

From acetic acid. *[For prepn. of C̄ from acetic acid (1:1010) by chlorination at 250-500°* without cat. (625), with Cl_2 in sunlight (32), in light from Hg quartz lamp (122), in silent electric discharge (123), or more usually in presence of catalysts (123) (124) (125) especially sulfur (124) (126) (127) (128) (129), red P (123) (124) (130), iodine (124), mixtures of red P + PCl_5 + I_2 (123) (124) (125) (131) (132) (133) (134), or in acetic anhydride (138) (139) at 100° or in vapor phase over $NiCl_2$ at 350° (140) see indic. refs.]

[For prepn. of C̄ from acetic acid (1:1010) by chlorination with SO_2Cl_2 at 115-120° and 4-5 atm. press. (135) or in pres. of a little acetyl chloride (136) or in presence of dibenzoyl peroxide in CCl_4 (70% yield (137)) see indic. refs.; for formn. of C̄ from AcOH + HCl on electrolysis see (141).]

From trichloroethylene. [For prepn. of C̄ from trichloroethylene (3:5170) with conc. H_2SO_4 at 190-195° see (142) (143) (144) (145) (146); for patents on this process see (147) (148) (149) (150) (151) (152) (153) (154). — Note also that H_2SO_4 may be replaced by arom. sulfonic acids such as benzenesulfonic acid see (155). — Note also that a very similar process (156) starting from *unsym.*-tetrachloroethane (3:5555) doubtless first involves loss of HCl to trichloroethylene.]

From other chloro-compounds. C̄ is also formed by appropriate oxidation of many suitably constituted chloro-compounds [e.g., for formn. of C̄ from 1,2-dichloroethane (ethylene (di)chloride) (3:5130) with dry O_2 in u.v. light see (157)].

[For formn. of C̄ by oxidation of unsaturated chloro-compds. see the following examples: 1,2-dichlorobutene-2, low-boilg. isomer (3:5360), high-boilg. isomer (3:5615) with $KMnO_4$ in acetone (158); 1,4-dichlorobutene-2 (3:5725) with $KMnO_4$ or O_3 (159); 1,2,4-trichlorobutene-2 (3:9062) with aq. $KMnO_4$ (160); 1,4-dichloro-2-methylbutene-2 (3:9204) with O_3 followed by $KMnO_4$ (161); 4-chlorobutadiene-1,2 (3:7225) with aq. alk. $KMnO_4$ (162); 1,3-dichlorohexadiene-2,4 (3:9310) with aq. $KMnO_4$ (163); 3,3,6-trichlorohexadiene-1,4 (3:9308) with aq. $KMnO_4$ (164); 1,3,4,6-tetrachlorohexadiene-2,4 (3:9306) with aq. $KMnO_4$ (164); 3,6-dichlorohexatriene-1,3,4 (3:9304) with aq. $KMnO_4$ (164); 1-chloro-5-methoxypentadiene-2,3 with aq. $KMnO_4$ (165); ethyl 5-chloropenten-3-oate with aq. $KMnO_4$ (166); 1-chloro-5-methoxy-5-phenylpentene-2 with $KMnO_4$ in acetone (35); chloroacetylene (3:7000) with NaOCl (167).]

[For formn. of C̄ from ethylene chlorohydrin (3:5552) by oxidn. with CrO_3 (168); from

1-chloropropanol-2 (propylene α-chlorohydrin) (3:7747) by oxidn. with HNO_3; from 1,3-dichloropropanol-2 (" α-dichlorohydrin ") (3:5985) by oxidn. with conc. HNO_3 (169) cf. (170) see indic. refs.]

[For formn. of $\bar{C}$ from chloroacetaldehyde (3:7212) by oxidn. with conc. HNO_3 (171) cf. (172), AgOH (172) or dil. H_2O_2 (173); from chloroacetone (3:5425) by oxidn. with $KMnO_4$ (161) (174), CrO_3 (174), HNO_3 (174), (175); from 1-chlorobutanone-2 (3:8012) by oxidn. with HNO_3 (176) (177) see indic. refs.]

From aminoacetic acid (glycine). [For formn of $\bar{C}$ from glycine with nitrous acid (40% yield (178)), with conc. HCl + conc. HNO_3 (179), or from glycine hydrochloride with satd. aq. $MgCl_2$, $CaCl_2$, or $ZnCl_2$ + $NaNO_2$ (180), see indic. refs]

From miscellaneous sources. [For prepn of $\bar{C}$ from ketene with Cl_2 in gas phase, CCl_4, or dry ether, followed by aq. (181); from ketene with aq $Ca(OCl)_2$ (182); from formaldehyde + CO + HCl gas at 180° and 800–900 atm. (183), for formn of $\bar{C}$ from α-trioxymethylene with SO_2Cl_2 in pres. of $ZnCl_2$ or $AlCl_3$ in s.t at 150° for 12 hrs (2); from methyl formate (1:1000) with SO_2Cl_2 in s.t. at 165–170° (2); from ethylene with ClO_2 (184); from nitro-trichloromethane (" chlorpicrin ") in AcOH on exposure to light (185) cf. (186) (187) (188)]

[For formn. of $\bar{C}$ from α,β-dichlorovinyl ethyl ether (3.5540) on boilg. with excess aq. see (189) (note, however, that with calcd. amt. aq. ethyl chloroacetate (3:5700) results (190)); for formn. of $\bar{C}$ from *unsym.*-tetrachloroacetone (3:6085) by hydrolytic cleavage with aq. KOH see (191).]

[For formation of $\bar{C}$ from its own derivatives, e g., chloroacetyl chloride (3:5235), chloroacetic acid anhydride (3:0730), methyl chloroacetate (3:5585), ethyl chloroacetate (3:5700), or other esters, etc., see these compds.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$

[$\bar{C}$ on distn. through a red-hot tube decomposes giving (192) HCl + CO + CH_2O (1:0145) + *sym.*-dichlorodimethyl ether (3:5245). — $\bar{C}$ at 250–340° over ThO_2, kaolin, or animal charcoal gives (193) HCl + CO + CO_2, but $\bar{C}$ merely boiled with activated carbon undergoes no decomposition (194).]

[$\bar{C}$ on htg. in tertiary bases such as dimethylaniline (195) or pyridine (196) decomposes into CO_2 + MeCl (3:7005), undoubtedly by way of formn. and decompn. of intermediate quaternary ammonium compds. (betaines) (196).]

[$\bar{C}$ in dry ether or C_6H_6 soln. on exposure to ultra-violet light decomposes giving (197) HCl + fumaric acid (1:0895) + a substance which on shaking with aq yields glycolide (1:0667).]

Reduction of $\bar{C}$

[$\bar{C}$ on reduction in aq. or aq. alc. alk. with H_2 in pres. of Pd or Ni (198) (199) (200), or $\bar{C}$ with chromous sulfate (201), or $\bar{C}$ with finely divided Fe (202), or $\bar{C}$ in aq EtOH in ultra-violet light (203), or $\bar{C}$ on electrolytic reduction (204) gives acetic acid (1:1010). — Note, however, that attempts to effect bimolecular hydrogenation of $\bar{C}$ to succinic acid have been unsuccessful (205).]

Oxidation of $\bar{C}$

[$\bar{C}$ on oxidn. with $K_2S_2O_8$ gives (206) methylene (di)chloride (3:5020); for study of oxidn. of $\bar{C}$ to CO_2 with $K_2S_2O_8$ see (207). — $\bar{C}$ (as Na$\bar{A}$) on electrolysis gives (208) cf. (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II$_1$-

(193)], and other prods. — For study of photochemical oxidn. of C̄ with $KMnO_4$ in pres. of uranyl salts see (210).]

Reactions Involving Substitution of H Atoms of Alkyl Radical of C̄

Fluorination. The behavior of C̄ with F_2 appears not to have been studied: chloro-fluoroacetic acid is unknown; chloro-difluoroacetic acid [Beil. II-201] although known has been prepd. from difluoroacetic acid by chlorination.

Chlorination. [C̄ with Cl_2 (211) in pres. of I_2 (212) gives dichloroacetic acid (3:6208) very likely accompanied by some trichloroacetic acid (3:1150).]

Bromination. [C̄ with Br_2 at 160° is claimed (213) to give chloro-bromo-acetic acid [Beil. II-217, II_2-(204)], but this is best prepared by other means, e g., from α,β-dichlorovinyl ethyl ether (3:5540) by addn. of Br_2, conversion by distn. to chloro-bromo-acetyl chloride, and hydrolysis (214) (41) (215) (216). — Note that although dibromination of C̄ to chloro-dibromo-acetic acid [Beil. II-220] appears unreported, yet this product is obtd. by other means cf. (217).]

Sulfonation. [C̄ with $ClSO_3H$ on warming (218) or C̄ with SO_3 finally at 70° (219) cf. (220) gives sulfo-chloroacetic acid [Beil. III-598, III_1-(208), III_2-(387)], hygroscopic ndls. of monohydrate from aq., m.p. 83° (219) (corresp. *bis*-acid chloride, oil, b.p. 70° at 3 mm., $D_{-}^{15} = 1.669$, $n_D^{23} = 1.4920$ (121); corresp. N,N,N',N'-tetraphenyldiamide, m.p. 210° (121)), accompanied (218) (220) by some chloromethanedisulfonic acid (chloromethionic acid) [Beil. II-25]. — For resolution of *d,l*-sulfochloroacetic acid see (219).]

Miscellaneous substitution reactions. [C̄ (as KĀ) on boilg. with aq. gives (222) the salt of chloromercuri-chloroacetic acid which with either acid or alk. gives glycolic acid (1:0430).]

Reactions Involving the —COOH Group of C̄

Acidic Strength of C̄

C̄ behaves as a very strong monobasic acid; Neut. Eq. = 94.5. — [Ionization const. of C̄ in aq. at 25° is 1.55×10^{-3} (223) (224), 1.51×10^{-3} (224) (225), 1.396×10^{-3} (226), 1.378×10^{-3} (227). — For examples of other studies of ioniz. const. of C̄ in aq. see (228) (229); for study of temp. variation of ioniz. const. in aq. over range 0–40° see (227) (230); for H^+ conc. of C̄ in aq. solns. (75), in aq. solns. of KCl or NaCl (231) (234), or in buffer mixts. of C̄ + NaĀ (232) (233); for studies of elec. conductivity of C̄ in aq. soln. at 0° (235), at 60° (236), at 62.5° (45), or over range 0–78° (4) see indic. refs. — For discussion of resonance and acid strength of C̄ see (237) (238) (239). — For study of "sourness" of C̄ from taste aspect see (252).]

[Studies of acid strength of C̄ in other solvents include the following: in EtOH (240) (241), in *n*-BuOH (24) (242), in 60% methyl "cellosolve" (ethylene glycol monomethyl ether) (243), in *m*-cresol (242), in ether (244), in formamide (245), in acetonitrile (246), in C_6H_6 (247), in chlorobenzene (248), or in $CHCl_3$ (244). — For studies on electrometric titration of C̄ in C_6H_6 (249), or use of indicators with C̄ in C_6H_6 soln. (250), see indic. refs. — For studies of elec. conductivity of C̄ in MeOH, EtOH, BuOH, acetone see (251).]

Catalytic Effect of C̄ upon Various Reactions

The catalytic influence of C̄ upon diversified types of chem. reaction has been extensively examined; although this matter cannot be recorded exhaustively, the following examples are cited.

[For studies of catalytic effect of C̄ upon the inversion of *l*-menthone to *d*-isomenthone in C_6H_6 (253) or in chlorobenzene (254); upon racemization of methyl-phenyl-acetophenone

and of isobutyl-phenyl-acetophenone in various solvents (255); upon I_2/acetone reaction (224) (234) (256) (257) (232); upon hydrogen disproportionation of limonene (622) see indic. refs.]

[For studies of catalytic effect of $\bar{C}$ upon the hydrolysis of ethyl formate in neutral salt solns. at 25° (258); of EtOAc (259) (235) in pres. of Na$\bar{A}$ or NaCl (259) (225); of sucrose (260) (261) see indic. refs.]

[For studies of catalytic effect of $\bar{C}$ upon formn. of ether from ethyl alcohol (262); upon depolymerization of paraldehyde (273) or of dimeric dihydroxyacetone (263); upon bromination of ethyl acetoacetate (264) see indic. refs.]

[For studies on catalytic effect of $\bar{C}$ upon nitration of toluene (265) (266); upon decompn. of ethyl diazoacetate in C_6H_6 (253) (267); upon decompn. of nitramide (268); upon rearr. of *N*-chloroacetanilide in chlorobenzene soln at 100° (269); upon rearr. of *N*-bromoacetanilide in chlorobenzene, C_6H_6, or ethylene (di)chloride (270); upon rearr. of *N*-iodoformanilide in anisole (271); upon rearr. of *N*-bromobenzanilide in chlorobenzene at 25° (272) see indic. refs.]

Salts of $\bar{C}$

This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [$NH_4\bar{A}$, from $\bar{C}$ in abs. alc. with dry NH_3 gas (274). — Hydroxylamine salt, $HONH_3\bar{A}$, cryst. from boilg. alc., m p. 124–125° (275).]

[Na$\bar{A}$ on electrolysis gives (208) (209) methylene (di)chloride (3:5020), chloromethyl chloroacetate [Beil. II-198, II$_1$-(193)], and other prods.; on htg. gives (276) polyglycolid, for rate of decompn. by aq. see (277). — K$\bar{A}$, $3H_2O$ (32); K$\bar{A}$ 1½H_2O (32) (277) (for study of rate of decompn. by aq. see (277)); K$\bar{A}$.$\bar{C}$, sparingly sol. aq (32). — Ag$\bar{A}$, spar. sol. cold aq., more readily in hot aq. (32); for soly. in HNO_3 see (278); dry htg. gives (279) AgCl + polyglycolid; on htg. with a little aq. gives (279) AgCl + glycolic acid; for prepn. and study of activity coefficient in pres. of electrolytes see (280); for sensitivity to light see (281).]

[Be$\bar{A}_2$, see (293); Mg$\bar{A}_2$.$2H_2O$, very sol. aq. or alc. (277); Ca$\bar{A}_2$.H_2O, very sol. aq. or alc. (277) (for use in eel worm control in soil see (282)); Sr$\bar{A}_2$, spar. sol. aq alc (277); Ba$\bar{A}_2$.H_2O (32) (277) (293) (for use in detn. of $\bar{C}$ see (121) (623)); Cu$\bar{A}_2$, $4H_2O$ (274), Cu$\bar{A}_2$.$3H_2O$ (283), Cu$\bar{A}_2$ (274) cf. (284); for study of electrolysis see (285); for dissoc see (288); for various complexes with NH_3 and amines see (286) (287). — Zn$\bar{A}_2$.2(4?)H_2O (274). — Cd$\bar{A}_2$ $6H_2O$, for prepn. (289), crystallography (290), dissociation (288), and conductivity (291) see indic. refs. — Pb$\bar{A}_2$, spar. sol. cold aq. (274). — Hg$\bar{A}_2$, spar. sol. aq. (292). — $Hg_2\bar{A}_2$, spar. sol. aq. (292).]

[Al$\bar{A}_3$, see (293). — Mn$\bar{A}_2$.$\bar{C}$.H_2O (274); Mn$\bar{A}_2$ $\bar{C}$.$2H_2O$ (274); Mn$\bar{A}_2$ $1.5H_2O$ (289). — Co$\bar{A}_2$.$6H_2O$, m.p. 68–69° (289), for study of complexes with pyridine see (294). — Ni$\bar{A}_2$, $3H_2O$ (274), for complexes with various amines see (295). — For studies on complexes of $\bar{C}$ with iron salts see (274) (296) (297).]

Salts with organic bases (amines). [*Aniline chloroacetate*, m p. 88° (298) (best from $\bar{C}$ in dry ether treated dropwise with aniline in dry ether with cooling (299); note that this salt with P_2O_5 on stdg. gives (299) ω-chloroacetanilide, m p 136° cor.). — *o-Toluidine chloroacetate*, m.p. 95° (300). — *p-Toluidine chloroacetate*, m.p. 97.5° (300) (note that this salt at 80–90° for 2 hrs. (301) or with P_2O_5 (302) gives chloroaceto-*p*-toluidide, m.p. 164° (302)).]

α-Phenylethylamine chloroacetate, from $\bar{C}$ + base in EtOAc, m.p 93.6–94.4° u.c., 94.7–95.5° cor. (303) — *Benzylamine chloroacetate*, from $\bar{C}$ + base in EtOAc, m p. 118.4–119.4° u.c., 119.9–120.9° cor. (303) (note that this m p. is practically identical with corresp benzylamine salt of trichloroacetic acid (3:1150) q v.). — *Piperazine bis-(chloroacetate)*, m.p 145–146° cor. (304). — *Semicarbazide chloroacetate*, m p. 111–112° (305).

Phenylhydrazine chloroacetate, from $\bar{C}$ with phenylhydrazine in C_6H_6, m.p. 111° (306) (note that this product is definitely the salt since on titration with alk. it gives Neut. Eq. 204.7 as against calcd. value of 202.6 (306); however, during detn. of m.p. it is undoubtedly converted to chloroaceto-phenylhydrazide, m.p. 115° (307), directly obtd. from chloroacetyl chloride (3:5235) with phenylhydrazine in ether (307)).

Behavior of Acidic Hydrogen of $\bar{C}$ with Metals

[For study of rate of soln. of Mg in aq. solns. of $\bar{C}$ see (308); for behavior of $\bar{C}$ with Zn see (309); for study of 20% aq. solns. of $\bar{C}$ on silver see (310).]

Esterification of $\bar{C}$

This book includes the following esters of $\bar{C}$ under their own individual numbers q.v.: *methyl chloroacetate* (3:5585), *ethyl chloroacetate* (3:5700), *n-propyl chloroacetate* (3:0565), *isopropyl chloroacetate* (3:8160), *n-butyl chloroacetate* (3:8530), *isobutyl chloroacetate* (3:8375) *sec-butyl chloroacetate* (3:8350), *ter-butyl chloroacetate* (3:8220), *ethylene glycol (mono)-chloroacetate* (3:6780), *ethylene glycol bis-(chloroacetate)* (3:0720), *β-methoxyethyl chloroacetate* (3:9285), *diethylene glycol (mono)chloroacetate* (3:9390), *triethylene glycol (mono)-chloroacetate* (3:9588), and *phenyl chloroacetate* (3:0565).

[For studies of rate of esterification of $\bar{C}$ under various conditions with MeOH (1:6120) (311) (312) (313) (314) (315), with EtOH (1:6130) (312) (313) (1) (316) (317) (318), with isobutyl alc. (1:6165) (319) (320), with amyl alc. (313), or with neopentyl alc. (1:5812) (321) see indic. refs. — For studies on esterification of $\bar{C}$ with alcohols by BF_3 method (312) (322) or without cat. (328) see indic. refs.]

[For patents involving esterification of $\bar{C}$ with alcs. (323) by use of Cl_2 (324) see indic. refs.]

[*For study of use of $\bar{C}$ in esterification of various carbohydrate derivs.* (325) *or of cellulose* (326) cf. (327). — Note that the chemistry of poly (vinyl chloroacetate) cannot be considered here.]

Addition Reactions of $\bar{C}$ with Organic Compounds

Addition to unsaturated linkages. $\bar{C}$ in presence of suitable cat. adds to unsaturated linkages giving the corresp. esters [e g., $\bar{C}$ with propylene + BF_3 at 60–70° gives (34.2% yield (329)) isopropyl chloroacetate (3:8160); $\bar{C}$ with butene-2 + $ZnCl_2$ at 100° for 8 hrs. gives (330) *sec*-butyl chloroacetate (3:8350); similarly $\bar{C}$ with pentene-2 (1:8215) gives (330) diethylcarbinyl chloroacetate, b.p. 177–178°. — Note, however, that no record can be found of reaction of $\bar{C}$ with ethylene to give ethyl chloroacetate (3:5700)].

[$\bar{C}$ with *n*-butylacetylene (hexyne-1) (1:8055) in pres. of HgO + MeOH + $BF_3.Et_2O$ gives (68% yield (331)) 2-(chloroacetoxy)hexene-1, b.p. 100–101° at 20 mm., $D^{25}_{-} = 1.017$, $n_D^{25} = 1.4453$ (331). (For addition of Br_2 to this prod. giving 67% yield 1-bromohexanone-2 + 21% yield chloroacetyl bromide see (334)).]

Addition to epoxy compounds. [$\bar{C}$ with ethylene oxide (1:6105) in dry ether at 0° for 4 days (332) or at 50° under press. for 6 days (333) gives ethylene glycol mono(chloroacetate) (3:6780).]

Conversion of $\bar{C}$ to Corresponding Acyl Halides

Conversion of $\bar{C}$ to chloroacetyl fluoride. [$\bar{C}$ on distn. with fluorosulfonic acid (335) or $\bar{C}$ with KF + benzoyl chloride (3:6240) (336) gives (yields: 30% (336), 15% (335)) chloroacetyl fluoride, b.p. 74° (335), 74–76° (336).]

Conversion of $\bar{C}$ to chloroacetyl chloride. [$\bar{C}$ can by numerous methods be converted

to chloroacetyl chloride (3:5235) q.v. — Note also, however, that $\bar{C}$ with large excess PCl_5 (4 moles) gives (337) tetrachloroethylene (3:5460) and other products.]

Conversion of $\bar{C}$ to chloroacetyl bromide. [$\bar{C}$ with Br_2 + red P (338) (339) or with PBr_3 (340) gives chloroacetyl bromide, b.p. 127° (338) (340), $D^{0}_{-} = 1.840$ (340).]

Conversion of $\bar{C}$ to Corresponding Anhydride

$\bar{C}$ can by numerous methods be converted to chloroacetic acid anhydride (3:0730) q.v.

Reactions Involving the Chlorine Atom of $\bar{C}$

Reduction of $\bar{C}$

See above as second heading under *chemical behavior of* $\bar{C}$.

Hydrolysis of $\bar{C}$ (or its salts)

Hydrolysis of $\bar{C}$ to glycolic (hydroxyacetic) acid (1:0430) together with the formn. under certain conditions of diglycolic acid (1:0495) has been very extensively studied.

Hydrolysis of $\bar{C}$ (or its salts) with aq. $\bar{C}$ on protracted boilg. with aq. (341) (342) (343) or $\bar{C}$ (as $Na\bar{A}$ or $K\bar{A}$) on boiling with aq. (32) (344) (277) or C with aq. $BaCO_3$ (followed by pptn. of barium with H_2SO_4 (345)) gives (88 7% yield (345)) glycolic acid (1:0430).

[For studies on rate of hydrolysis of $\bar{C}$ by aq. under various conditions (626) (342) (343) (346) (347) (348) (349) (350) (351), for study of influence of ultra-violet light (352) (353) (354) (355); for influence of temperature (356); for study of ord. and in heavy aq. (357); for heat of hydrolysis with aq. (358); for study of abnormalities of hydrolysis of salts (359); for study of induction period of hydrolysis (360) (383); for acceleration of hydrolysis by colloidal Ag, Ag_2O, or CuO (349) see indic. refs.]

[For studies of quantum yields of hydrolysis of $\bar{C}$ and use as standard see (361) (362) (363) (364) (365) (366) (367) (353).]

Hydrolysis of $\bar{C}$ (or its salts) with alkalies. $\bar{C}$ on hydrolysis with aq alkalies also gives glycolic acid (1:0430) [for studies of this reaction see (368) (342) (346) (369) (370) (350) (371) (351) (372) (373); for studies of hydrol. of $Na\bar{A}$ by salts of weak acids (374), for study of basic catalysts (375), for effect of high press. (376) see indic. refs.]

[For patents on conversion of $\bar{C}$ to glycolic acid (1:0430) by alkaline hydrolysis see (377) (378); note, however, that the glycolic acid so formed may be converted (379) to glycolid (1:0667).]

Note also that under the influence of the alkaline medium some of the glycolic acid first formed may condense with unreacted $\bar{C}$ to give diglycolic acid (1:0495): for studies of this aspect of the reaction see (380) (381) (382).

Behavior of $\bar{C}$ with NaSH or Its Relatives

[$\bar{C}$ with aq. 15% KSH (384) or with freshly prepd. aq. 15% NaSH (385) at 95° for 1 hr., subsequently acidified with H_2SO_4 and extracted with ether, gives (90% yield (385)) mercaptoacetic acid (thioglycolic acid) {Beil. III-244, III_1-(95), III_2-(175)}, b p. 107-108° at 16 mm. (384) (385), m.p. = −16.5° (384), $D^{20}_{20} = 1.3253$ (384) — Note that this prod. is also preparable by many other methods some of which are cited below.]

[$\bar{C}$ (2 moles) as $Na\bar{A}$ with NaSH as directed (386) (387) (388), or as $K\bar{A}$ with KSH (389) (390), or as $Na\bar{A}$ with potassium sulfantimonite (391) or sodium sulfostannate (391), or as $Ca\bar{A}_2$ with excess $Ca(SH)_2 + H_2S$ (381) gives (84% yield (387)) thiodiglycolic acid (thiodiacetic acid), $S(CH_2COOH)_2$ {Beil. III-253, III_1-(97), III_2-(178)}, cryst. from $AcOEt/C_6H_6$ (1:9) (388) m p. 130° (389), 129° (387) (386).]

[C̄ (2 moles) as NaĀ with aq. Na_2S_2 (392) (393) (394), with alk. or alk.-earth polysulfides (402), with sodium sulfantimonate Na_3SbS_4 (391) or sodium sulfarsenate Na_3AsS_4 (391) gives dithiodiglycolic acid, $HOOC.CH_2—S—S—CH_2COOH$ [Beil. III-254, III_1-(97), III_2-(179)], lfts. from $AcOEt/C_6H_6$ (1:9) (388) 108–109° (391), 106° (388). — Note that this prod. on reduction gives mercaptoacetic acid (above): e.g., for reduction with Sn + HCl (395), with Zn + H_2SO_4 (393) (396) (401) (402), with Na/Hg (397), by electrolytic reduction in H_2SO_4 soln. using Pb electrodes (398), by shaking soln. of sodium salt with Fe powder at 38° under N_2 (399), or by shaking with alanine or phenylalanine in 1% soln. in pres. of active carbon at 38° under N_2 (400) see indic. refs.]

Behavior of C̄ with Various Salts of Inorganic Acids

(For behavior with NaCN, etc., see further below.)

With halides. [C̄ with $HBr.5H_2O$ in s.t. at 150° gives (403) bromoacetic acid [Beil. II-213, II_1-(95), II_2-(201)], m.p. 49–50°, b.p. 208°; however, C̄ in aq. KBr at 50° shows only very slight tendency to formn. of bromoacetic acid (for study of equilibrium see (404)).]

[C̄ with aq. KI at 50° (405) (406), or C̄ with NaI in acetone at room temp. (407) (or in ethyl methyl ketone, diethyl ketone, or AcOEt (407) but *not* in EtOH (408)) gives iodoacetic acid, cryst. from much pet. ether (405) (409), m.p. 83° (405), 82° (406); for study of equilibrium of C̄ with KI in aq. at 50° see (404); of C̄ with KI or NaI in acetone (ionic reaction) see (410).]

With salts of inorganic sulfur, nitrogen, or phosphorus acids. [C̄ with aq. Na_2SO_3 gives (41) (412) salts of sulfoacetic acid [Beil. IV-21, IV_1-(312), IV_2-(531)]; for study of rate of reaction of KĀ with Na_2SO_3, K_2SO_3, or $(NH_4)_2SO_3$ under various conditions see (214) (413).]

[The salts of C̄ with aq. $Na_2S_2O_3$ give the corresp. salts of "glycolic acid thiosulfate" (carboxymethyl hydrogen sulfate) [Beil. III-235, III_1-(97), III_2-(171)]; for studies of this reaction see (414) (415) (416) (417) (418).]

The alkali salts of C̄ with aq. alkali nitrites give the corresp. alkali salts of nitroacetic acid; in fact from a conc. aq. soln. of the potassium nitroacetate, treatment with the calcd. amt. of conc. HCl and extraction with much ether gives (70% yield (419)) (420) free nitroacetic acid [Beil. II-225, II_1-(99), II_2-(207)], m.p. 87–89° dec. (420). — However, even aq. solns. of the alkali salts of nitroacetic acid on warming readily lose CO_2 yielding nitromethane [Beil. I-74, I_1-(19), I_2-(40)], b.p. 100.80–100.86° at 760 mm. (421), f.p. −29.2°, D_4^{25} = 1.1322 (421), n_D^{22} = 1.38056 (421), and although this product is now commercially available from other sources, the reaction is of considerable interest in connection with C̄. — [For studies on the prepn. of nitromethane from KĀ + KNO_2 (yield 47% (422)) (423) (424) or from NaĀ + $NaNO_2$ (yields: 70% (428), 58% (426), 53% (429) (430) (431), 35–38% (425)) see indic. refs. — For studies on rate of decompn. of nitroacetic acid in aq. soln. at 20° (432), in HCl, or in acetate buffered solns. at 17.84° and 9.78° (433) cf. (434) (435) (436) see indic. refs.]

[The behavior of C̄ with NaN_3 appears to be unreported; note, however, that ethyl chloroacetate (3:5700) with NaN_3 gives (437) ethyl azidoacetate [Beil. II-229, II_1-(101), II_2-(208)], which upon hydrolysis with aq. KOH gives (437) azidoacetic acid.]

[For behavior of C̄ with aq. Na_3PO_4 at 85° see (438).]

Behavior of C̄ with Hydrocarbons

C̄ with certain aromatic hydrocarbons or their halogen derivs. at elevated temp. but without cat. condenses with elimination of HCl to give arylated acetic acids [e.g., C̄ with

naphthalene (1:7200) at 180–185° for 48 hrs. gives (439) α-naphthylacetic acid (1:0728)); $\bar{C}$ with 1-chloronaphthalene (3:6878) in generally similar fashion gives (440) 1-chloronaphthalene-?-acetic acid, m.p. 124°; for generally analogous behavior of $\bar{C}$ with acenaphthene, anthracene, fluorene, and even certain phenols and amines see (440).]

Behavior of Chlorine Atom of $\bar{C}$ with Organic OH and SH Reactants

With alkoxides. $\bar{C}$ with excess alkali alkoxides condenses with elimination of alkali chloride to give the corresponding alkoxyacetic acids [e.g., $\bar{C}$ with MeOH/NaOMe (440) (441) or probably also MeOH/Ba(OMe)$_2$ cf. (442) gives methoxyacetic acid (1:1065); $\bar{C}$ with abs. EtOH/NaOEt (2 moles) gives (yields: 93% (441), 90% (443), 74% (444)) ethoxyacetic acid (1:1070); $\bar{C}$ with NaO-n-Pr in n-PrOH gives (64% yield (445)) n-propoxyacetic acid [Beil. III-233, III$_1$-(90), III$_2$-(170)], b.p. 123° at 20 mm. (446), 108° at 10 mm. (445), D_4^{20} = 1.0518 (446), n_D^{22} = 1.42219 (446); $\bar{C}$ with NaO-n-Bu gives (84% yield (445)) (447) n-butoxyacetic acid [Beil. III$_1$-(90), III$_2$-(170)], b.p. 115–116° at 10 mm. (445), 113–114° at 9–10 mm. (447), D_4^{20} = 1.0213 (447), n_D^{20} = 1.42031 (447); $\bar{C}$ with Na isobutylate gives (441) isobutoxyacetic acid [Beil. III-233, III$_1$-(90)], b.p. 118° at 18 mm. (441), 114° at 9 mm. (447), D_4^{20} = 1.0074 (447), n_D^{20} = 1.42001 (446); for analogous behavior of $\bar{C}$ with sodium derivs. of n-amyl alc. (1:6205) (445), n-hexyl alc. (1:6230) (446), n-heptyl alc. (1:6240) (445) (448), n-octyl alc. (1:6255) (445), octanol-2 (1:6245) (446) cf. (449), geraniol (1:6270) (448), l-menthol (1:5940) giving (yields: 78–84% (450), 80% (451), 75% (452)) l-menthoxyacetic acid [Beil. VI$_1$-(25)], m.p. 53–54° (452), benzyl alc. (1:6480) giving (75% yield (453)) (448) benzyloxyacetic acid; etc., see indic. refs.]

With alkali salts of mercaptans. $\bar{C}$ with alkali salts of mercaptans should give the [illegible] have been prepd. by alkylation [illegible] with NaSMe should give methyl- [illegible] mm. (454), 123–124° at 20 mm. [illegible] cpn. has not been reported, the [illegible] m thioglycolate by methylation]. — $\bar{C}$ (as Na$\bar{A}$) with NaSEt in conc. aq. soln. followed by acidification gives (456) ethylmercaptoacetic acid [Beil. III-248, III$_1$-(95)], b.p. 117–118° at 11 mm. (456), 118–119° at 10 mm. (455), m.p. −8.7° (456), D_4^{20} = 1.1497 (456). — [illegible] acid, b.p. 136.5–137° at 18 mm. (455), 132° at 15 mm. [illegible] 1.483 (454), and isopropylmercaptoacetic acid, b.p. 128 [illegible] 9 mm. (455), have been reported only by alkylation of thioglycolic acid. — However, $\bar{C}$ (as Na$\bar{A}$) with Na-S-n-C_4H_9 in aq. soln. gives (yields: 90% (457), 87% (458)) n-butylmercaptoacetic acid, b.p. 144–145° at 14 mm. (455) (corresp. p-bromophenacyl ester, m.p. 95° (458)), for constants on the isomeric isobutyl (455) (459), sec.-butyl (455), and $tert$-butyl (460) mercaptoacetic acids prepd. by other means see indic. refs. — $\bar{C}$ (as Na$\bar{A}$) with NaS-n-C_7H_{15} gives (461) n-heptylmercaptoacetic acid.]

With phenols. $\bar{C}$ (as Na$\bar{A}$) with salts of phenols, or often $\bar{C}$ with phenols in aq. alk. soln., reacts to give the corresp. aryloxyacetic acids; this procedure comprises a valuable tool for derivatization in the identification (462) of phenols. Although the products of reaction of $\bar{C}$ with all possible phenols cannot be recorded here, attention is directed to the 44 aryloxyacetic acids derived from phenols of Order 1 comprising the summary on page 641 of the "Tables of Order 1" (464), and to analogous aryl oxyacetic acids occurring in this present book as follows: o-chlorophenoxyacetic acid (3:4260); m-chlorophenoxyacetic acid (3:3325); p-chlorophenoxyacetic acid (3:4375); 2,4-dichlorophenoxyacetic acid (3:4095); 2,4,5-trichlorophenoxyacetic acid (3:4335). Many other individual cases which cannot be mentioned here may be found by the usual search methods.

Behavior of C̄ with Salts of Organic Acids

With NaCN, KCN, etc. [C̄ on conversion to NaĀ and reaction with aq. NaCN (465) (466) (475) (476) or KCN (467) (468) (469) gives (yields: 75% (469), 70% (468)) cyanoacetic acid (malonic acid mononitrile) [Beil. II-583, II_1-(253), II_2-(530)], m.p. 69–70° (468), 69° (470), 66.1–66.4° cor. (467), 65–66° (471), 65° (472) (473); for use of this reaction in prepn. of malonic acid (1:0480) see (476).]

Note, however, that the behavior of C̄ or its salts with KSCN, NH_4SeN, alkali xanthates, etc., is both complex and disputed and cannot be detailed here.

Behavior of C̄ with NH_3

C̄ with NH_3 under various conditions gives aminoacetic acid (glycine) [Beil. IV-333, IV_1-(462), IV_2-(771)].

[For behavior of C̄ with conc. aq. NH_4OH as method of prepn. of glycine (yields: 66–69% (477), 64–65% (478), 54% (479), 50% (480)) (481) (482) (486) (for numerous older refs. see Beilstein) see indic. refs.: for extensive studies on influence of conditions on this reaction see (483) (477); for study of rate of ammonolysis of C̄ see (484) (485). — For behavior of C̄ with liq. NH_3 see (487); note that C̄ in liq. NH_3 with Na splits out calcd. amt. NaCl and that *no* cyanide is formed (488). — For behavior of C̄ with $(NH_4)_2CO_3$ see (483) (477) (489).]

[Note that reaction of C̄ with NH_3 does not stop with formn. of aminoacetic acid (glycine) but that unchanged C̄ reacts with the latter to give (489) (490) (480) iminodiacetic acid ("diglycolamidic acid") $HN(CH_2COOH)_2$ [Beil. IV-365, IV_1-(481), IV_2-(800)], and/or trimethylamine-α,α',α''-tricarboxylic acid ("triglycolamidic acid") [Beil. IV-369, IV_1-(482), IV_2-(801)], also obtd. from C̄ on fusion with $ZnCl_2/NH_3$ (492).]

Behavior of C̄ with Organic Amines

With primary aliphatic amines. [C̄ with $MeNH_2$ as directed (497) gives (methylamino)-acetic acid (*N*-methylglycine = sarcosine) [Beil. IV-345, IV_1-(468), IV_2-(784)], but this prod. is usually prepd. in other ways. — Note, however, that C̄ (2 moles) with $MeNH_2$ (1 mole) + excess aq. NaOH gives (63–71% yield (493)) (494) methyliminodiacetic acid, $CH_3N(CH_2COOH)_2$ [Beil. IV-367, IV_2-(800)], cryst. from aq. MeOH, m.p. 226–227° dec. (495), 226° dec. (496).]

[*C̄ with excess aq. $EtNH_2$ as directed (498) gives* ethylaminoacetic acid (*N*-ethylglycine) [Beil. IV-349, IV_2-(787)], m.p. 180–182° dec. (499), 181.5° dec. (500). — The homologous *N*-alkylglycines appear never to have been prepared from similar reaction of C̄ with alkylamines, but for prepn. of *N*-(*n*-propyl)glycine [Beil. IV-352], m.p. 196–198° dec. (499), *N*-(isopropyl)glycine [Beil. IV_2-(787)], *N*-(*n*-butyl)glycine, m.p. 192° (501), *N*-(isobutyl)-glycine, m.p. 188° (501), or *N*-(*n*-amyl)glycine, m.p. 201° (501), by other methods see indic. refs.]

With secondary aliphatic amines. [C̄ with aq. Me_2NH (502) (29) for 4 hrs. at 55° under press. (503) or with aq. N
aminoacetic acid (*N*,*N*-d
182° (29), 176–178° (503)
hyde see (505)). — C̄ with Et_2NH similarly gives (506) *N*,*N*-diethylglycine [Beil. IV-350, IV_1-(472)].]

With tertiary aliphatic amines. [C̄ with Me_3N (507) or C̄ (as NaĀ) with Me_3N (508) gives betaine hydrochloride $(CH_3)_3N(Cl).CH_2COOH$ [Beil. IV-347, IV_1-(470), IV_2-(786)].]

With primary aromatic amines. (See also below under Ⓟ's.) [C̄ with aniline in a little ether boiled with a large volume of aq. (509), cf. (511), or C̄ with aniline (3 moles) boiled with aq. and subsequently made alkaline (510), or best C̄ with aq. aniline heated in presence

of an acid acceptor such as aq. NaOH (512), aq. NaOAc (573) cf. (514), or other alkali or alkaline-earth hydroxides or carbonates (515) (516) (517) (518) (519) gives (yields: 100% (514), 90% (516), 86% (512)) phenylaminoacetic acid (*N*-phenylglycine) [Beil. XII-468, XII_1-(263)], m.p. 127° (note that if htd. at 200°, however, bimolecular condensation occurs with elimination of $2H_2O$ and formn. (520) (521) of *N,N'*-diphenyl-2,5-diketopiperazine, m.p. 263° (520) (521) while distn. causes loss of CO_2 giving (522) *N*-methylaniline). — Note also that reaction of $\bar{C}$ with 2 moles aniline (523), or further reaction of $\bar{C}$ with *N*-phenylglycine (above) in aq. alk. (524) (525) (514) (526), gives (yields: 80–85% (526), 50–60% (525)) phenylimino-diacetic acid, $C_6H_5N(CH_2COOH)_2$ [Beil. XII-480, XII_1-(265)], m.p. 152–155° dec. (526). — Note also that reaction of $\bar{C}$ with aniline in pres. of NaOAc gives (525) much *N*-phenylglycine anilide, $C_6H_5NHCH_2CONH.C_6H_5$ [Beil. XII-556], m.p. 112°.]

[Note that $\bar{C}$ with many other primary aromatic amines reacts in analogous fashion, but details cannot be included here because of lack of space.]

With primary aromatic diamines. [$\bar{C}$ with *o*-phenylenediamine in dry ether forms (327) a 1:1 cpd. presumably to be regarded as salt. — However, $\bar{C}$ (1 mole) with *o*-phenylenediamine (1 mole) in 4 *N* HCl refluxed (528) for 45 min. *and allowed to stand overnight* (529) (530) gives (yields: 80–85% (529), 78–86% (530)) 2-(chloromethyl)benzimidazole, ndls. from EtOH/AcOEt (528), pr. from dioxane (529) or dry acetone (530), m.p. 165° (529), 160–161° (528), 159–160° cor. (530), note that value is sensitive to rate of htg. (529) (530). — For studies of behavior of this product with many amines (529) (530), with aq. (530), KI in acetone (530) (531) see indic. refs. — For general study of ortho condensations leading to benzimidazole formn. see (532).]

With hydrazines. [$\bar{C}$ (1 mole) with phenylhydrazine (2 moles) in boilg. aq. alc. K_2CO_3 (½ mole) gives (533) (534) a mixt. of both (α-phenylhydrazino)acetic acid, $C_6H_5N(NH_2)$-CH_2COOH [Beil. XV-316], tbls. from abs. EtOH, m.p. 168° (533), 167° dec. (535), and (β-phenylhydrazino)acetic acid, $C_6H_5NH.NHCH_2COOH$ [Beil. XV-321], lfts. from alc., m.p. 153° (536), 152–153° (537); for separation of these isomers see (533).]

[For behavior of $\bar{C}$ with *N,N*-diphenylhydrazine in aq. Na_2CO_3 or NaOAc see (538).]

With aromatic primary amines also containing other functional groups. *With aminophenols.* [$\bar{C}$ with *p*-aminophenol on htg. in aq. soln. (539) (540) (541) (542) contg. also NaOAc (543) (544) gives (yields: 45% (544), 35% (539) *N*-(*p*-hydroxyphenyl)glycine [Beil. XIII-488, $XIII_1$-(171)] (this product has considerable interest as a photographic developer); for its purification see (540) (545); for pat. on its decompn. at 160–170° in ketone solvents as method of prepn. of *N*-methyl-*p*-aminophenol [Beil. XIII-441, $XIII_1$-(149)] see (546). — Note also that in above reaction of $\bar{C}$ with *p*-aminophenol some *N*-(*p*-hydroxyphenyl)iminodiacetic acid (542) is also formed.]

With amino acids. [$\bar{C}$ with *o*-aminobenzoic (anthranilic) acid in aq. soln. (547) preferably also contg. Na_2CO_3 (548) (549) (550) gives (yields. 85–89% (550), 70–80% (549)) *N*-(*o*-carboxyphenyl)glycine (phenylglycine-*o*-carboxylic acid) [Beil. XIV-348, XIV_1-(544)], ndls. from MeOH, m.p. about 215° dec. (551); this product upon htg. loses CO_2 giving indoxyl and is therefore an important intermediate in mfg. of indigo; for use of this reaction for detection of $\bar{C}$ in wine by conversion to indigo see (120) cf. (117). — Note also that in above reaction of $\bar{C}$ with anthranilic acid some *N*-(*o*-carboxyphenyl)iminodiacetic acid [Beil. XIV-354, XIV_1-(545)], m.p. 216° dec. (551), is also produced (551); although both phenylglycine-*o*-carboxylic acid (Neut. Eq. 97.5) and *N*-(*o*-carboxyphenyl)-iminodiacetic acid (Neut. Eq. 84.3) thus melt at same temp., their mixture melts at about 200° (551).]

With secondary aromatic amines. [$\bar{C}$ with *N*-methylaniline on htg. (552) or better in aq. NaOH on 4-hr. reflux (553) gives (74% yield (553)) *N*-methyl-*N*-phenylglycine [Beil. XII-473, XII_1-(264)], oil (B.HCl, m.p. 215–216° dec. (553)). — $\bar{C}$ with *N*-ethylaniline on

htg. gives (554) *N*-ethyl-*N*-phenylglycine [Beil. XII-475], oil. — $\bar{C}$ with diphenylamine at 180–200° for 40–50 hrs. gives (5–10% yield (555)) *N*,*N*-diphenylglycine [Beil. XII_1-(264)].]

With tertiary aromatic amines. [$\bar{C}$ with dimethylaniline at 100° (556) for 12–18 hrs. (557) gives dimethyl-phenylbetaine hydrochloride [Beil. XII-474], m.p. 194–196° (556), from which silver oxide liberates (557) (558) free dimethyl-phenyl-betaine, m.p. 124–126° (557), 123–124° (558). — For corresp. betaine from *N*,*N*-diethylaniline see (559).]

With tertiary heterocyclic amines. [$\bar{C}$ with pyridine on htg. (560) (561) (194) cf. (556) at 60° for 5 hrs. (557) gives *N*-(carboxymethyl)pyridinium chloride (pyridinebetaine hydrochloride) [Beil. XX-226], m.p. 202–205° dec. (560) (thought by (194) to be typographical error for 102–105° dec.). — For behavior of $\bar{C}$ with quinoline see (556).]

Behavior of $\bar{C}$ with Amides, Thioamides, etc.

This topic cannot here be treated in full, but the following cases are reported as examples.

With urea. [$\bar{C}$ with carbamide (urea) might be expected under appropriate conditions to condense with elimination of HCl and formn. of ureidoacetic acid (hydantoic acid), $NH_2CONH.CH_2COOH$ [Beil. IV-359, IV_1-(477), IV_2-(792)], m.p. 169–170° (562) (563), 160–161° (564), 160° (565), or its ring-closure product hydantoin [Beil. XXIV-242, $XXIV_1$-(287)], m.p. 220°; no report of the chemical behavior of $\bar{C}$ with urea can be found, however, the two above-mentioned expected products having been prepared by other means. — Note that f.p./compn. data on system $\bar{C}$ + urea have been recorded (19).]

With thiourea. [$\bar{C}$ with thiourea (the latter reacting in its isothiourea mode) gives according to conditions either isothiohydantoic acid, $H_2N—C(=NH)—S—CH_2.COOH$ [Beil. III-251, III_1-(97)] (566) (567), or pseudothiohydantoin [Beil. XXVII-233, $XXVII_1$-(303)], (568) (569) (570) (571) (572) (573).]

With substituted thioureas. The behavior of $\bar{C}$ with substituted thioureas cannot be treated in full, but the following examples are cited [for reaction of $\bar{C}$ with various monosubstituted thioureas see (573) (574), with various disubstituted thioureas see (575) (576) (577)].

—— Methyl chloroacetate: oil, b.p. 131° (see 3:5585).

—— Ethyl chloroacetate: oil, b.p. 144° (see 3:5700).

—— Phenyl chloroacetate: m.p. 44–45° (see 3:0565).

—— *o*-Tolyl chloroacetate: oil, b.p. 127–127.6° at 10 mm. (578). [From $\bar{C}$ with *o*-cresol (1:1400) + $POCl_3$ in pyridine (574), or from chloroacetyl chloride (3:5235) with *o*-cresol (1:1400) at 130° for 4 hrs. (578); note that this prod. with $AlCl_3$ at 140° undergoes Fries rearr. giving (578) both 2-hydroxy-3-methylphenacyl chloride [Beil. $VIII_1$-(549)], m.p. 67°, and 4-hydroxy-3-methylphenacyl chloride [Beil. $VIII_1$-(550)], m.p. 144–145°.]

—— *m*-Tolyl chloroacetate: oil, b.p. 153° at 30 mm. (580). [From chloroacetyl chloride (3:5235) with *m*-cresol (1:1730) (579) (580); note that this prod. with $AlCl_3$ at 150° gives (50% yield (580)) 2-hydroxy-4-methylphenacyl chloride [Beil. VIII-113, $VIII_1$-(550)], m.p. 101°.]

—— *p*-Tolyl chloroacetate: m.p. 32° (580), 29–30° (579); b.p. 162° at 45 mm. (580); $D_4^{35} = 1.1840$ (41), $n_D^{35} = 1.5150$ (41). [From $\bar{C}$ with *p*-cresol (1:1410) + $POCl_3$ in pyridine (579), or from chloroacetyl chloride (3:5235) with *p*-cresol (1:1410) at 135° (580); note that this prod with $AlCl_3$ at 140° gives (580) 2-hydroxy-5-methylphenacyl chloride [Beil. VIII-111], m.p. 65° (580).]

—— Benzyl chloroacetate: oil, b.p. 147.5° at 9 mm., $D_4^4 = 1.2223$, $n_D^{18} = 1.5246$ (581). [From $\bar{C}$ with benzyl alc. (1:6480) + HCl gas at 100° (581).]

— *p*-Nitrobenzyl chloroacetate: oil, unsuitable as Ⓓ (582).
— Phenacyl chloroacetate: unreported.
— *p*-Chlorophenacyl chloroacetate: unreported.
Ⓓ *p*-Bromophenacyl chloroacetate: m.p. 103.7° cor. (583).
— *p*-Iodophenacyl chloroacetate: unreported.
Ⓓ *p*-Phenylphenacyl chloroacetate: m.p. 116° (584). [From C̄ (as $Na\bar{A}$) with *p*-phenylphenacyl bromide (584) (m.p. 124.5–125.5°) in aq. alc. on htg. (584).]
Ⓓ *S*-Benzylthiuronium chloroacetate: m.p. 159–160° (585). [Note that for corresp. salts from dichloroacetic acid (3:6208) and trichloroacetic acid (3:1150) m.p. values are respectively 178–179° and 148–149° (585).]
Ⓓ *S*-(*p*-Chlorobenzyl)thiuronium chloroacetate: m.p. 158° cor. (586). [From C̄ (as $Na\bar{A}$) with *S*-(*p*-chlorobenzyl)thiuronium chloride (586) (m.p. 197°) in alc. (586); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 148° cor.]
Ⓓ *S*-(*p*-Bromobenzyl)thiuronium chloroacetate: m.p. 154° cor. (587). [From C̄ (as $Na\bar{A}$) with *S*-(*p*-bromobenzyl)thiuronium bromide (587) (m.p. 213°) in alc. (587); note that corresp. deriv. of trichloroacetic acid (3:1150) has m.p. 146° cor. (587).]
Ⓓ ω-Chloroacetamide: m.p. 120.5–121.5° (588), 120° (589), 119–120° (590), 119.5° (591), 118–120° (165), 118° (312), 116.4–116.9° (620). [From methyl chloroacetate (3:5385) (588) (593) or ethyl chloroacetate (3:5700) (590) (589) (592) (594) (595) (596) (597) with cold conc. NH_4OH (78–84% yield (590)), or from chloroacetyl chloride (3:5235) with dry NH_3 (597).]
Ⓓ ω-Chloroacetanilide: cryst. from hot aq. or 50% alc., m.p. 138° cor. (598), 136–137° (599), 136° cor. (600), 135° (601), 134–135° (602) (166), 134.5° (603) (604), 134° (605) (606), 133–134° (610). [From C̄ with aniline (606) in presence of P_2O_5 (600) (605), from C̄ with aniline salts + PCl_3 or $SOCl_2$ (607), from chloroacetyl chloride (3:5235) with aniline (2 moles) in ether (608) (603), C_6H_6 (602) (601), or AcOH/NaOAc (599) or with aniline (1 mole) + aq. NaOH in C_6H_6 or toluene (609), or from chloroacetic acid anhydride (3:0730) with aniline + P_2O_5 (610).] Note that this ω-chloroacetanilide with $AlCl_3$ (not more than 1.8 pts. (611)) at 225° (611) (612) loses HCl with ring closure giving (85% yield (611) (612)) oxindole [Beil. XXI-282, XXI₁-(289)]; also that ω-chloroacetanilide with alc. KOH undergoes bimolecular condensation giving (613) *N*,*N'*-diphenyl-2,5-diketopiperazine, m.p. 263°.]
Ⓓ ω-Chloroacet-*o*-toluidide: cryst. from dil. alc., m.p. 111–112° (614) (604), 111° (615). [From C̄ + *o*-toluidine + P_2O_5 (615), or from chloroacetyl chloride (3:5235) with *o*-toluidine (2 moles) in dry ether (616) or C_6H_6 (614).] [Note that this prod. with $AlCl_3$ at 225° loses HCl with ring closure giving (612) 7-methyloxindole, m.p. 200°, also that with alc. KOH it undergoes bimolecular condensation giving (614) *N*,*N'*-di-*o*-tolyl-2,5-diketopiperazine.]
Ⓓ ω-Chloroacet-*p*-toluidide: m.p. 164° (615), 162° (608) (617), 161.5° (603). [From C̄ (2 moles) with *p*-toluidine (1 mole) at 80–90° (617) in presence of P_2O_5 (615), or from chloroacetyl chloride (3:5235) with *p*-toluidine (2 moles) (608) in ether (603).] [Note that this prod. with $AlCl_3$ at 230° for 2 hrs. loses HCl with ring closure giving (612) 5-methyloxindole [Beil. XXI-291], m.p. 168° (612).]
— ω-Chloroacet-*N*-benzylamide: cryst. from C_6H_6 or lgr., m.p. 93.5–94.5° cor. (618), 93.0–93.6° cor. (619), 92.2–92.8° u.c. (619). [From ethyl chloroacetate (3:5700) with aq. benzylamine on shaking in cold (619) cf. (621), or from chloroacetyl chloride (3:5235) with benzylamine + aq. KOH (618); note, however, that the corresp. derivs. from dichloroacetic acid (3:6208) and from trichloroacetic acid (3:1150) have almost the same m.p.'s, viz., 93.8–95.6° cor. and 94.6–94.4° cor. respectively (619); note also that the simple salt of C̄ with benzylamine has m.p. 119.9–120.9° cor. (619).]

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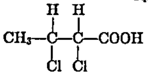
3:1375 α,β-DICHLORO-n-BUTYRIC ACID (low-melting isomer) (Crotonic acid dichloride) $C_4H_6O_2Cl_2$ Beil. II - 279 II_1-(124) II_2—



M.P. 63°	(1) (2) (3) (6)	B.P. 132–133° cor.	at 27 mm.	(5)
		124.5°	at 20 mm.	(6)
62.5–63°	(4)			
62°	(8)	124–125°	at 20 mm.	(1)
61°	(11)	120°	at 13 mm.	(9)
57–59°	(5)			

[*See also α,β-dichloro-n-butyric acid (high-melting isomer) (isocrotonic acid dichloride)* (3:1903).]

Colorless cryst. from pet. ether, lgr. or dry ether. — $\bar{C}$ is eas. sol. alc., C_6H_6, $CHCl_3$, or CS_2; spar. sol. cold lgr.; at 10.5° 3.28 pts. $\bar{C}$ are sol. in 1 part dry ether. — $\bar{C}$ deliquesces with a little aq. (5); $\bar{C}$ with 1 mole H_2O forms (4) an oil, probably a monohydrate (ortho acid), which in much aq. gives an emulsion gradually separating into two clear layers; note, however, that $\bar{C}$ has later (11) been claimed to be nonhygroscopic.

[For prepn. of $\bar{C}$ from crotonic acid (1:0425) with Cl_2 in CS_2 (1) (2) (3) (4) (11) or in $CCl_4 + CS_2$ (6) in cold see indic. refs.; for formn. of $\bar{C}$ from isocrotonic acid (1:1045) with Cl_2 in $CHCl_3$, CCl_4, or CS_2 see (6) (4); for prepn. of $\bar{C}$ from its corresp. acid chloride (see below) by hydrolysis with aq. $NaHCO_3$ see (5) (9).]

$\bar{C}$ boils at 212–216° under ord. press. with some loss of HCl (4).

[$\bar{C}$ with 6 pts. conc. aq. HCl (satd. at 0°) in s.t. at 100° for 50 hrs. (1) is partially isomerized *to the high-melting stereoisomer (isocrotonic acid dichloride) (3:1903).*]

$\bar{C}$ behaves as a fairly strong monobasic acid of ionization const. $K = 8\,2 \times 10^{-3}$ (1); $\bar{C}$ with dil. aq. $AgNO_3$ ppts. the spar. sol. $Ag\bar{A}_2$ (5); no other salts, however, appear to have been reported.

$\bar{C}$ with aq. NaOH in cold is neutralized without serious decomposition (4); Neut. Eq. = 157 (11); however, if to the resulting soln. further conc. aq. NaOH is added (4) (7), or if $\bar{C}$ in alc. is treated with alc. KOH (6) (2), 1 HCl is split away and the corresp. salt of α-chloroisocrotonic acid (3:1615) (accompanied by the salt of its isomeric α-chlorocrotonic acid (3:2760)) is formed.

$\bar{C}$ with aq. Na_2CO_3 at ord. temp. is neutralized without decompn. (4); however, $\bar{C}$ with excess aq. Na_2CO_3 above 80° also is further attacked giving (4) (25–30% yield (4)) 1-chloropropene-1 (3:7030), accompanied by some propionaldehyde (1:0110), α-chlorocrotonic acid (3:2760), α-chloroisocrotonic acid (3:1615), and other products.

$\bar{C}$ in pyridine at 100° for 3 hrs. loses HCl giving (yield not reported (8)) α-chlorocrotonic acid (3:2760), m.p. 99.5° (8).

[$\bar{C}$ with PCl_5 or $SOCl_2$, although not actually reported, would be expected to yield the corresp. acid chloride; this α,β-dichloro-n-butyryl chloride, b.p. 163.3–164.3° cor. at 747 mm. (5), 67.5–71° at 30 mm. (5), has, however, been prepd. indirectly from crotonic acid (1:0425) with PCl_5 (2 moles) at 160° for 2 hrs. (9) or from crotonaldehyde (1:0150) with Cl_2 at 0° in dark (5).]

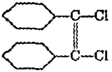
—— Methyl α,β-dichloro-n-butyrate: b.p. 174–180° sl. dec. at ord. press. (5), 82.7–85.7° cor. at 28 mm. (5); $D_4^{18.3} = 1.2614$ (5). [From the above α,β-dichloro-n-butyryl chloride with MeOH (5).]

—— Ethyl α,β-dichloro-n-butyrate: b.p. 180–200° at 760 mm. (10), 97° at 35 mm. (10), 96° at 35 mm (2). [From C̄ in abs. EtOH with dry HCl (2), or indirectly from butyrchloral hydrate (3:1905) (1 mole) in EtOH with dry KCN (1 mole) below 15° (10); note, however, that this ester loses HCl with great ease even at ord. temp. giving ethyl α-chlorocrotonate (3:8523) and this dehydrohalogenation is greatly accelerated by KCN (10).]

—— α,β-Dichloro-n-butyramide: unreported. [Note that the amide from the higher-melting stereoisomer of C̄ (3:1003) has m p. 121°.]

3:1375 (1) Michael, Bunge, *Ber* **41**, 2910–2912 (1908). (2) Michael, Browne, *Am. Chem. J.* **9**, 281–287 (1887). (3) Michael, Browne, *J. prakt Chem* (2) **36**, 174–176 (1887). (4) Wislicenus, *Ann.* **248**, 281–301 (1888). (5) Zeisel, *Monatsh.* **7**, 360–370 (1886). (6) Michael, Schulthess, *J. prakt. Chem* (2) **46**, 238–240, 255–259 (1892). (7) Wislicenus, *Ber.* **20**, 1008–1010 (1887). (8) Pfeiffer, *Ber* **43**, 3041–3042 (1910). (9) Clarke, *J. Chem. Soc.* **97**, 898 (1910). (10) Chattaway, Irvine, *J. Chem Soc.* **1929**, 1043–1044.
(11) Stelling, *Z. physik. Chem.* **B-24**, 427 (1934).

3:1380 ***cis*-1,2-DICHLORO-1,2-DIPHENYLETHYLENE** (*cis*-α,α'-Dichlorostilbene; *cis*-tolane dichloride)



$C_{14}H_{10}Cl_2$ Beil. V - 634, V_1-(304), V_2—

M.P. 63° (1) (2) (3) (4) (5) (6) (7) (8)
62–63° (9)
62° (10)
61° (11)
60° (12)
59.5–60° (13)
58° (14)

B.P. 178° at 18 mm. (5)

[*See also trans-1,2-dichloro-1,2-diphenylethylene* (3·4210).]

Colorless ndls — C̄ is much less sol in alc. than its higher-melting stereoisomer (3:4210); 100 pts abs. alc. at 24.4° dis 10 51 pts. C̄ (14). — C̄ like its isomer is very sol. in ether.

Note that C̄ (the lower-melting tolane dichloride) has now been shown (12) to have the *cis* configuration, many earlier reports to the contrary notwithstanding.

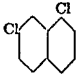
Note also that C̄ (2 moles) with (1 mole) diphenylacetylene (tolane) [Beil. V-656, V_1-(319), V_2-(568)], m.p. 60°, gives (12) a 2·1 molecular cpd., m.p. 67–69° (12).

C̄ on distn. is partially transformed (32% (14)) into its higher-melting *trans* stereoisomer (3:4210) q.v.

Since the methods of prepn. and the chemical behavior of C̄ are the same as those given in detail under its stereoisomer (3:4210) q.v they are not repeated here.

3:1380 (1) Fuson, Ross, *J Am. Chem. Soc.* **55**, 723 (1933) (2) Davidson, *J. Am. Chem. Soc.* **40**, 397–399 (1918) (3) Sudborough, *J. Chem. Soc* **71**, 221–222 (1897). (4) Lachowicz, *Ber.* **17**, 1165 (1884). (5) Blank, *Ann.* **248**, 17–25, 33–34 (1888). (6) Liebermann, Homeyer, *Ber.* **12**, 1973–1974 (1879) (7) Limpricht, Schwanert, *Ber* **4**, 379 (1871). (8) Zinin, *Ber.* **4**, 289 (1871). (9) Staudinger, *Ber.* **49**, 1971–1972 (1916). (10) Onufrowicz, *Ber.* **17**, 835 (1884).
(11) Busch, Weber, *J. prakt Chem.* (2) **146**, 50–52 (1936). (12) Bergmann, *J. Chem. Soc* **1936**, 403, 405. (13) Stelling, *Z. physik. Chem.* **B-24**, 425 (1934). (14) Eiloart, *Am. Chem. J.* **12**, 231–253 (1890).

3:1385 1,7-DICHLORONAPHTHALENE (2,8-Dichloronaphthalene)



$C_{10}H_6Cl_2$ Beil. V - 543, V_1-(263), V_2-(446)

M.P.		B.P.		
64°	(19)	286° u.c.	(5)	$D_4^{99.5} = 1.2611$ (19)
63.5–64.5°	(1)	285–286°	(2)	$n_D^{99.5} = 1.60921$ (19)
63.5–64°	(2)			
62.5°	(3) (18)			
61.5° u.c.	(4) (5) (9) (12) (13)			
61°	(8) (12)			

Lfts. from hot dil. alc.; cryst. from alc., ether, C_6H_6, or AcOH. — Sublimes readily. — Volatile with steam.

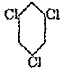
[For prepn. of C̄ from 7-chloronaphthalenesulfonyl chloride-1 [Beil. XI-161] (4), from 7-bromonaphthalenesulfonyl chloride-1 [Beil. XI-166] (6), from 1-chloronaphthalenesulfonyl chloride-7 [Beil. XI-181] (2), from 7-chloro-1-nitronaphthalene [Beil. V-556] (poor yield (2)) (7), from 1-nitronaphthalenesulfonyl chloride-7 [Beil. XI-187] (8) (9) (10) (11), from 7-chloronaphthol-1 [Beil. VI-612, VI_1-(308)] (12), from K or Na naphthol-2-sulfonate-8 [Beil. XI-286, XI_1-(67)] (5) (13), or from naphthalene-1,7-*bis*-(sulfonyl chloride) [Beil. XI-215] (14) on htg. with PCl_5 as directed see indic. refs.: from α-chloronaphthalene (3:6878) with SO_2Cl_2 at 100–180° see (15); from K 4,5-dichloronaphthalenesulfonate-2 [Beil. XI-182] or from K 4,6-dichloronaphthalenesulfonate-2 [Beil. XI-182] on hydrolysis in H_2SO_4 or H_3PO_4 with superhtd. steam see (16); from 4,6-dichloronaphthalene-2-sulfonyl chloride [Beil. XI-182] on htg. with conc. HCl in s.t. at 290° see (16); from 7-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and htg. with Cu_2Cl_2 see (12); from 8-sulfonaphthylamine-2 [Beil. XIV-750, XIV_1-(733)] via diazotization and htg. the diazonium salt with PCl_5 in PCl_3 see (2); from 1,7-diaminonaphthalene [Beil. XIII-204] via tetrazotization and treatment with Cu pdr. see (17).]

C̄ (1 g.) in AcOH (5 ml.) with highest concn. HNO_3 (2 ml.) yields (3) 1,7-dichloro-*x*-nitronaphthalene [Beil. V-556], ndls. from MeOH, m.p. 138–139° (3).

[C̄ with $ClSO_3H$ yields (1) (18) 1,7-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 118° (1) (18), corresp. sulfonamide, m.p. 226° (18)).]

3:1385 (1) Hampson, Weissberger, *J. Chem. Soc.* **1936**, 394. (2) Armstrong, Wynne, *Chem. News* **59**, 189 (1889). (3) Erdmann, *Ann.* **275**, 257 (1893). (4) Arnell, *Bull. soc. chim.* (2) **45**, 184 (1886). (5) Claus, Volz, *Ber.* **18**, 3157 (1885). (6) Sindall, *Chem. News* **60**, 58 (1889). (7) Armstrong, Wynne, *Chem. News* **59**, 225 (1889). (8) Palmaer, *Ber.* **21**, 3261 (1888). (9) [illegible] (1889).
[illegible] (1888).
[illegible] (15)
[illegible] *ews* **76**, 69–70 (1897). (17) Friedländer, Szymanski, *Ber.* **25**, 2083 (1892). (18) Armstrong, Wynne, *Chem. News* **61**, 274–275 (1890). (19) Krollpfeiffer, *Ann.* **430**, 198, 204 (1923).

3:1400 1,3,5-TRICHLOROBENZENE (*sym.*-Trichlorobenzene)



$C_6H_3Cl_3$

Beil. V - 204
V_1-(43)
V_2-(156)

M.P. 63.0–63.8°	(1)	B.P. 208.5° cor. at 763.8 mm.	(2)
63.5° cor.	(2)	208.4°	(11)
	(3) (18)		
63.4° cor.	(4)		
63°	(5) (6)		
	(7) (8)		
62.7°	(9)		
61°	(10)		

Colorless cryst.; eas sol. ether, C_6H_6, lgr , CS_2; spar. sol. cold alc. or 50% AcOH; volatile with steam. [For thermal anal of mixts. of C̄ with 1,2,4-trichlorobenzene (3:6420) or for m.p /compn. data on ternary system of C̄ with 1,2,3-trichlorobenzene (3:0990) and 1,2,4-trichlorobenzene (3:6420) see (9).]

[For use of C̄ in mfg. of electric insulating material see (12) (13).]

[For prepn. of C̄ from 2,4,6-trichloroaniline [Beil. XII-627, XII_1-(312)] via diazotization and reaction with alc. (yield: 92% (14), 90% (15), 72.6% (8), 67% (33)) (4) (1) (16) (17), or from 2,4,6-tribromoaniline [Beil XII-663, XII_1-(329)] via diazotization and subsequent treatment with HCl gas in alc. (18), see indic. refs.; from 3,5-dichloroaniline [Beil. XII-626, XII_1-(312)] via diazotization and reaction with Cu_2Cl_2 or Cu (yield 58% (5), 40–50% (9)) (4) see indic. refs ; from chlorobenzene-3,5-disulfonyl chloride with 4 moles PCl_5 in s.t. at 200–210° for 4 hrs. (60% yield (6)) or similarly from bromobenzene-3,5-disulfonyl chloride (7) see indic. refs.]

[For formn. of C̄ from 2,4,6-trichloroiodobenzene with alc. NaOEt see (19); from 1,3,5-trinitrobenzene with conc. HCl in s.t. at 260° see (20); from 2,4,6-trichloroacetophenone on fusion with KOH (10) or from 2,4,6-trichlorobenzaldehyde on warming with 50% NaOH or KOH (3) see indic. refs ; from chloroacetylene (3:7000) by polymerization in light see (21), for formn. of C̄ from C_6H_6 or chlorobenzene (3:7903) with Cl_2 at 400–700° (22), or from mixt. of *m*- and *p*-dichlorobenzenes with Cl_2 + $AlCl_3$ (23) cf. (24), or from hexachlorobenzene (3:4939) by cat. hydrogenation (25) see indic. refs.; from α-benzene-hexachloride (3:4410) with alc. KOH, pyridine, or quinoline (9) from β- or γ-benzene-hexachlorides with alc. KOH see (9) cf. (26).]

[C̄ with Cl_2 in pres. of Al/Hg yields (27) 1,2,3,5-tetrachlorobenzene (3:0915); for behavior of C̄ with liq. Cl_2 yielding addn. products see (28).]

[C̄ with MeOH/NaOMe in s t. at 180° yields mainly (29) 3,5-dichloroanisole, m.p. 39° (29), accompanied by some 3,5-dichlorophenol (3:1670).]

[C̄ on hydrolysis with steam at 550–800° over cat yields (30) phloroglucinol (1:1620); for behavior of C̄ with F_2 see (31); for behavior of C̄ with NH_3 at 700–800° see (32).]

C̄ on mononitration, e g., by warming C̄ (1 g) with 5 ml fumg. HNO_3 (D = 1.49) at 100° for 15 min., then pouring onto ice (38), gives (2) (8) (100% yield (38)) 1,3,5-trichloro-2-nitrobenzene [Beil. V-247], ndls. from alc., m.p 69° (8), 67–68° (38). — C̄ on dinitration, e g , by refluxing for 1 hr. a soln. of C̄ (1 g.) in 5 ml. fumg. HNO_3 (D = 1.49) + 5 ml. conc. H_2SO_4 (38), gives (yield: 100% (38) (34), 82% (35), 80% (15)) (14) (33) 1,3,5-trichloro-2,4-dinitrobenzene [Beil. V-265], m p 131–131.5° (35) (36), 129–130° (34), 129 5° (14) (15) (3), 128 5° (38) (this prod. on htg. with 5 pts. aniline yields (38) 1,3,5-trianilino-2,4-dinitrobenzene, m.p. 179–180° (38)). — C̄ on trinitration, e g., by boilg. 2 days with mixt. of

fumg. HNO_3 and fumg. H_2SO_4 as directed (37) (39), yields (37) (33) (17) 1,3,5-trichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p. 187° (33), 193° (15), 192–193° (39).

C̄ with conc. H_2SO_4 is unchanged even after htg. 56 hrs. at 100° and is only partially sulfonated on htg. 6 hrs. at 100° with fumg. H_2SO_4 (12% SO_3) (16); however, C̄ with 3 pts. fumg. H_2SO_4 (SO_3 = 72%) htd. at 100° for 15 hrs. completely sulfonates yielding (16) 1,3,5-trichlorobenzene-2,4-disulfonic acid (corresp. disulfonyl chloride, m.p. 161.5° (16), corresp. disulfonamide, m.p. 248° (16)).

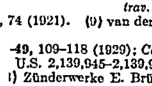
C̄ with chlorosulfonic acid in $CHCl_3$ (38) gives 1,3,5-trichlorobenzenesulfonyl chloride, *m.p. 35–40° u.c. (38); this prod. with $(NH_4)_2CO_3$ readily yields (38) 1,3,5-trichlorobenzene*-sulfonamide, m.p. 210–212° u.c. dec. (38).

432–433 (1932). (2) Beilstein, Kurba-
2 (1933). (4) Körner, *Gazz. chim. ital.*
197–198 (1918). (6) Olivier, *Rec. trav.*
trav. chim. **39**, 643 (1920). (8) Holleman, van Haeften, *Rec. trav. chim.* **40**, 74 (1921). (9) van der Linden, *Ber.* **45**, 231–247 (1912).

-49, 109–118 (1929); *Cent.* **1929**, II 2162. (12) Ford (to
U.S. 2,139,945–2,139,948, Dec. 13, 1938; *Cent.* **1939**, I
) Zünderwerke E. Brünn, A.G., Ger. 570,460, Feb. 16, 1933; *Cent.* **1933**, I 2770. (14) Jackson, Lamar, *Am. Chem. J.* **18**, 667–668 (1896). (15) Backer,
1177–1178 (1937). (16) Davies, Poole, *J. Chem. Soc.* **1927**,
& industrie **26**, 781–794 (1931). (18) Hantzsch, *Ber.* **30**,
olo, Am. Chem. J. 22, 53–54 (1899). (20) Lobry de Bruyn,
(1896).
1536 (1924). (22) Wibaut, van der Lande, Wallagh (to Dow
23) Mouney-
-413 (1920).
(27) Cohen,
–324 (1936).
Cent. **1932**,

(31) Bancroft, Whearty, *Proc. Natl. Acad. Sci.* **17**, 183–186 (1931). (32) Heslinga, *Rec. trav. chim.* **43**, 178–180 (1924). (33) Jackson,
Rec. trav. chim. **40**, 451 (1921). (35) S
Borsche, Trautner, *Ann.* **447**, 6 (1926).
(38) Huntress, Carten, *J. Am. Chem. S*
u. Sprengstoffw. Nitrocellulose **38**, 198–199 (1943); *C.A.* **38**, 3962 (1944).

3:1420 1,1,1-TRICHLORO-2,2-DIPHENYLETHANE



$C_{14}H_{11}Cl_3$

Beil. V - 606
V_1-(285)
V_2-(510)

M.P. 64° (1) (2) (3)
63–64° (5)

Colorless lfts. from alc. — 100 pts. 90–92% alc. dis. at room temp. 5.40 pts. C̄; in hot 37.28 pts. C̄ (4).

[For prepn. of C̄ from chloral (3:5210) with C_6H_6 (2 moles) + conc. H_2SO_4 (almost quant. yield) see (3); from chloral hydrate (3:1270) with C_6H_6 + a little $AlCl_3$ at 0° see (5) cf. (2); note that both types of this same condensation take place through intermediate formn. of trichloromethyl-phenyl-carbinol [Beil. VI-476, VI_1-(237)], m.p. 37°, b.p. 145° at 15 mm. (1) (corresp. acetate, m.p. 87.5° (1)) as formerly suspected (6) and subsequently confirmed (1).]

C̄ on reduction gives various products according to conditions [e.g., C̄ with Na/Hg in

alc. is claimed (7) to give 1,1-diphenylethane [Beil. V-605, V_1-(285), V_2-(509)], but this prod. was not obtd. in pure form and was accompanied by 1,1-dichloro-2,2-diphenylethylene (3:1938) (from $\bar{C}$ by loss of HCl under alk. conditions)].

[$\bar{C}$ in boilg. 95% alc. contg. trace of $CuCl_2$ with finely powdered Al/Cu/Zn (Devarda) alloy or Cu/Mg (Arnd) alloy for 6–10 hrs. gives (13–19% yield (8)) 2,2,3,3-tetrachloro-1,1,4,4 tetraphenylbutane [Beil V_2-(676)], ndls from AcOH, m.p. 188–190° (8), accompanied by some 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 (see next paragraph). $\bar{C}$ with Zn dust + conc. aq. NH_4OH in alc. soln gives (18) (4) stilbene (1:7250) + 1,1-diphenylethane (above).]

[$\bar{C}$ on reduction with H_2 in pres. of Pd/$BaCO_3$ in alc./pyridine soln. gives (54–60% yield (9)) 2,2,3,3-tetrachloro-1,1,4,4-tetraphenylbutane (see preceding paragraph) accompanied by both high-melting (137–138°) and low-melting (108–110°) stereoisomers of 2,3-dichloro-1,1,4,4-tetraphenylbutene-2 [Beil. V_2-(685)]; using Ni as cat. the same prods. result (9) in lower yield sometimes accompanied also by 1,1-dichloro2,2-diphenylethylene (3:1938) (from $\bar{C}$ by loss of HCl)]

[$\bar{C}$ on reduction by electrolytic means in various types of solution, with various metallic electrodes, and at various temperatures gives (10) (11) numerous products including 1,1-dichloro-2,2-diphenylethane (3:1938), 1-chloro-2,2-diphenylethane [Beil V-606, V_1-(285)], 1,1,4,4-tetraphenylbutine-2 [Beil. V_1-(379), V_2-(694)], etc.; for details see (10) (11).]

[$\bar{C}$ with Cl_2 under suitable conditions should give 1,1,1,2-tetrachloro-2,2-diphenylethane [Beil. V-606], m p. 85°, but this reaction has not actually been reported — However, $\bar{C}$ with a very large excess (15 pts.) pure liquid Br_2 gives (12) 2-bromo-1,1,1-trichloro-2,2-diphenylethane, m.p. 87.5° (12)]

[No mono- or di-nitration products derived from $\bar{C}$ have been reported.]

$\bar{C}$ on distillation (13), or on boilg. with alc KOH (2) (14) (for study of rate see (15)), or during course of other reactions involving alkaline conditions (see above) loses HCl giving 1,1-dichloro-2,2-diphenylethylene (3:1938), m.p. 80° (2).

[$\bar{C}$ with NaOEt in s.t. at 180° ultimately gives (2) cf. (16) (and presumably through intermediate 1,1-dichloro-2,2-diphenylethylene (3:1938)) diphenylacetic acid (1:0765).]

$\bar{C}$ with Na in C_6H_6 refluxed 10–12 hrs. and then treated with alc. gives (17) cf. (2) *trans*-1,2-diphenylethylene (stilbene) (1:7250), m.p. 124°, *cis*-1,2-diphenylethylene (isostilbene) [Beil. V-633, V_1-(303), V_2-(539)], and diphenylacetylene (tolane) [Beil. V-656, V_1-(319), V_2-(568)]. — $\bar{C}$ with Zn dust on dry distn. gives (13) stilbene (1:7250).

[$\bar{C}$ in C_6H_6 with $AlCl_3$ gives (10% yield (20)) 1,1,2,2-tetraphenylethane [Beil. V-739, V_1-(371), V_2-(673)], m p. 211°.]

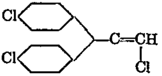
[For use of $\bar{C}$ as addn. agent to improve lubricating power of mineral oils under high pressures see (19).]

3:1420 (1) Chattaway, Muir, *J. Chem. Soc.* **1934**, 701–703 (2) Harris, Frankforter, *J. Am. Chem. Soc.* **48**, 3144–3150 (1926). (3) Baeyer, *Ber* **5**, 1098–1099 (1872). (4) Elbs, *J. prakt. Chem.* (2) **47**, 45–46, 77 (1893). (5) Frankforter, Kritchevsky, *J Am. Chem. Soc.* **36**, 1515–1518 (1914). (6) Dinesmann, *Compt. rend* **141**, 201 (1905). (7) Goldschmiedt, *Ber.* **6**, 1502–1503 (1873). (8) Brand, *Ber.* **54**, 1995–1996 (1921). (9) Brand, Horn, *J. prakt. Chem.* (2) **115**, 359–362 (1926). (10) Brand, *Z. Elektrochem.* **16**, 669 (1910); *Ber.* **54**, 2017 (1921).

(11) Brand, *Ber.* **46**, 2935–2942 (1913). (12) Schlenk, *Ann.* **493**, 213 (1912). (13) Goldschmiedt, *Ber.* **6**, 987, 990 (1873). (14) Baeyer, *Ber.* **6**, 223 (1873). (15) Brand, Busse-Sunder- [illegible]

3:1430 1-CHLORO-2,2-*bis*-(*p*-CHLOROPHENYL)ETHYLENE

$C_{14}H_9Cl_3$ Beil. S.N. 480



M.P. 64–65° (1)

Cryst. from lgr. — Note that C̄ may occur as a minor impurity in technical grade " DDT " (3:*3298*).

[For prepn. of C̄ from " *p,p'*-DDD " (3:3320) by elimination of 1 HCl with alc. KOH (77% yield) see (1).]

C̄ on oxidn. with CrO_3 gives (84% yield (1)) 4,4'-dichlorobenzophenone (3:4270).

3:1430 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

3:1445 α-CHLOROACRYLIC ACID

$CH_2{=}C(Cl){-}COOH$ $C_3H_3O_2Cl$ Beil. I - 401, I₁—, I₂—

M.P. 65° u.c. (1) (4)
64–66° (7)
64–65° (2) (3) (6)

Cryst. from pet. ether (2), ndls. from ether (1). — Eas. volatile, subliming even at room temp. (1) (4); volatile with steam.

[For prepn. of C̄ from α,α-dichloropropionic acid (3:6162) with alc. KOH see (4); from methyl α,β-dichloropropionate (3:9103) with aq. $Ba(OH)_2$ (62% yield (2)) (1) or alc. KOH (5) see indic. refs.; from α-chloro-β-hydroxypropionic acid (α-chlorohydracrylic acid) [Beil. III-298] by distn. with H_2SO_4 see (6) (7); from trichloroethylene (3:5170) with formaldehyde or paraformaldehyde + H_2SO_4 as directed see (3).]

C̄ on treatment with Ag_2O dec. yielding (1) Ag + AgCl.

C̄ with fumg. HCl in s.t. at 100° yields (5) (4) α,β-dichloropropionic acid (3:0855), m.p. 50°.

[The esters of C̄ (usually prepd. from the corresp. alkyl α,β-dichloropropionates by elimination of HCl) have assumed special importance because of their ability to polymerize to useful resins; for methyl α-chloroacrylate see 3:9096; for ethyl α-chloroacrylate see 3:9242; for *sec*-butyl α-chloroacrylate, and its mechanism of polymerization, see (8) (9); for studies on the electrical properties of β-chloroethyl α-chloroacrylate see (10).]

C̄ readily polymerizes in ultra-violet light or in pres. of peroxides (2).

3:1445 (1) Werigo, Werner, *Ann.* **170**, 168–171 (1874). (2) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940). (3) Imperial Chem. Ind., Ltd., French 845,230, Aug. 16, 1939; *C.A.* **35**, 1070 (1941); Brit. 528,761, Nov. 6, 1940; *C.A.* **35**, 7975 (1941). (4) Otto, Beckurts, *Ber.* **18**, 241–246 (1885). (5) Werigo, Melikov, *Ber.* **10**, 1499–1500 (1877). (6)

3:1460 3,4-DICHLOROPHENOL

$C_6H_4OCl_2$ **Beil. VI - 190**
VI_1-(103)
VI_2-(179)

M.P. 65° (1) (3) **B.P. 253.5°** at 767 mm. (2)
68° (2)

Ndls. (from C_6H_6 by addn. of pet. ether (2)). — Volatile with steam (1). [For study of ionization const see (4).]

[illegible] on see (2) (3) (5) (1).]
(2-chloroquinizarin)
[B [illegible] $_3$ at 195–200° see (7) (8); for use of $\bar{C}$ in prepn. of tetrachlorofluoran [Beil. XIX-148], m p. 255°, by htg. with phthalic anhydride see (3).]

$\bar{C}$ dis. eas. in conc. H_2SO_4; on stdg small pl of 3,4-dichlorophenol-6-sulfonic acid separate; these are sol. in aq., alc, AcOH, EtOAc; insol. in C_6H_6, pet eth.; spar. sol. $CHCl_3$; cryst. from latter, m p. 75–76° (6).

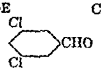
$\bar{C}$ on htg with mixt of fumg. H_2SO_4 (25% SO_3) + conc. H_2SO_4, and resultant solid treated with conc. HNO_3 ($D = 1.5$) as directed (1) gives (69% yield (1)) of 3,4-dichloro-2-nitrophenol, yel ndls., from lt. pet. ether, m.p. 76° (1).

$\bar{C}$ dislvd. in 3 pts. AcOH contg. anhyd. NaOAc, treated with Cl_2 and the prod. pptd. by addn. of aq., yields (5) 2,3,4-trichlorophenol (3:2185)

$\bar{C}$ dislvd. in aq. NaOH and shaken with $(CH_3)_2SO_4$ yields (2) the methyl ether, 3,4-dichloroanisole, m.p. −8° (2).

3:1460 (1) Hodgson, Kershaw, *J. Chem. Soc.* **1929**, 2922. (2) Holleman, *Rec. trav. chim.* **37**, 102–104 (1918). (3) Badische Anilin- und Soda-Fabrik, Ger. 156,333, Nov. 14, 1904; *Cent.* **1904**, II 1673. (4) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935) (5) Groves, Turner, Sharp, *J. Chem. Soc* **1929**, 523. (6) Kraay, *Rec trav. chim.* **48**, 1084–1085 (1930). (7) Gubelmann, Lee (to Newport Co), U S. 1,655,462, Jan. 10, 1928, *Cent.* **1929**, I 3149. (8) Gubelmann, U.S. 1,655,863, Jan. 10, 1928, *C.A.* **22**, 966 (1928).

3:1475 3,5-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ **Beil. S.N. 635**



M.P. 65° (1) **B.P. 235–240°** at 748 mm. (1)

Colorless ndls. or lfts. from pet. ether or dil MeOH (1). — Spar. sol. hot aq. but eas. volatile with steam — Eas. sol. most organic solvents.

[For prepn. of $\bar{C}$ from 3,5-dichlorotoluene (3:6310) via chlorination to 3,5-dichlorobenzal (di)chloride (3:0370) and subsequent hydrolysis with conc. H_2SO_4 (70–80% overall yield) see (1) (4).]

$\bar{C}$ with satd. aq $NaHSO_3$ yields a cpd. $\bar{C}$ $NaHSO_3$; this is exceptionally sol. in aq., and on htg. the soln. yields $\bar{C}$ (1)

$\bar{C}$ on oxidn. with excess $KMnO_4$ at 100° gives (74% yield (1)) 3,5-dichlorobenzoic acid (3:4840), m p. 188° (1). — $\bar{C}$ with 50% aq. KOH for 4 hrs. at 100° gives (90% yield (1)) 3,5-dichlorobenzyl alc., cryst. from C_6H_6, m p. 82° (1), and 3,5-dichlorobenzoic ac. (90% yield (1)) (3:4840).

$\bar{C}$ with PCl_5 gives (80% yield (1)) 3,5-dichlorobenzal (di)chloride (3:0370) cryst. from MeOH or dil. AcOH, m.p. 36.5° (1).

$\bar{C}$ on nitration with fumg. HNO_3 (D = 1.48) at 0° as directed (2) gives (99% *yield* (2)) 3,5-dichloro-2-nitrobenzaldehyde, cryst. from AcOH or lgr., m.p. 91.5° (2), 91° (4). [This deriv. yields an oxime, m.p. 97°, a phenylhydrazone, m.p. 175°, and on oxidn. with $KMnO_4$ gives 3,5-dichloro-2-nitrobenzoic ac., m.p. 194° cor. (2).]

$\bar{C}$ htd. with NaOAc + Ac_2O for 18 hrs. at 180–210° gives (76% yield (1)) 3,5-dichlorocinnamic acid, ndls. from C_6H_6 + pet. eth. or from dil. AcOH, m.p. 176° cor. (1).

[For conversion of $\bar{C}$ to 3,5-dichlorostyrene (5) (6) in a reaction with MeMgI giving (*yields*: 69% (5), 55% (3)) *3,5-dichlorophenyl-methyl-carbinol*, m.p. 46° (3), b.p. 126° at 4 mm. (5), n_D^{20} = 1.5573 (5), and dehydration of latter with $KHSO_4$ (43% yield (5)) see indic. refs.]

Ⓓ **3,5-Dichlorobenzaldoxime:** cryst. from lgr., C_6H_6 + pet. eth., or dil. AcOH, m.p. 112° (1).

Ⓓ **3,5-Dichlorobenzaldehyde phenylhydrazone:** yel. ndls. from pet. eth., m.p. 106.5° (1).

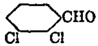
—— **3,5-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** unrecorded.

—— **3,5-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.

—— **3,5-Dichlorobenzaldehyde semicarbazone:** unrecorded.

3:1475 (1) Asinger, Lock, *Monatsh.* **62**, 344–348 (1933). (2) Asinger, *Monatsh.* **63**, 386–387 (1934). (3) Lock, Böck, *Ber.* **70**, 922–923 (1937). (4) Ruggli, Zaeslin, Lang, *Helv. Chim. Acta* **21**, 1247 (1938). (5) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 864 (1946). (6) Michalek, Clark, *Chem. & Eng. News* **22**, 1559–1563 (1944).

3:1480 2,3-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. S.N. 635



M.P. 65–67° (1)

Cryst. from 1:1 aq. EtOH.

[For prepn. of $\bar{C}$ from 2,3-dichlorotoluene (3:6345) by bromination at 180–200° (presumably to 2,3-dichlorobenzal (di)bromide) followed by hydrolysis with conc. H_2SO_4 at *100–140° (71% yield) see (1).*]

$\bar{C}$ with MeMgI gives (76% yield (1)) 2,3-dichlorophenyl-methyl-carbinol, m.p. 55–57°, b.p. 112–113° at 2 mm. (corresp. 3,5-dinitrobenzoate, m.p. 145–146° (1)); note that dehydration of the carbinol with $KHSO_4$ gives (44% yield (1)) 2,3-dichlorostyrene.

—— **2,3-Dichlorobenzaldoxime:** unreported.

—— **2,3-Dichlorobenzaldehyde phenylhydrazone:** unreported.

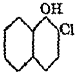
—— **2,3-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.

—— **2,3-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unreported.

—— **2,3-Dichlorobenzaldehyde semicarbazone:** unreported.

3:1480 (1) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 862 (1946).

3:1490 2-CHLORONAPHTHOL-1



$C_{10}H_7OCl$ Beil. VI - 611
VI_1-(308)
VI_2-(581)

M.P. 65° (1)
64–65° (2)

Ndls. from lgr.; exceptionally easily sol. in alc., ether, C_6H_6. — More volatile with steam than the isomeric 4-chloronaphthol-1 (3:3720) (use in sepn. (2)).

[For prepn. of Č from α-naphthol (1:1500) with aq. alk. NaOCl (3) (4) (5) or with SO_2Cl_2 in $CHCl_3$ soln. (18% yield, together with 42% yield of 4-chloronaphthol-1 (3:3720) (2)), see indic. refs.; from sodium 1-hydroxynaphthalenesulfonate-2 [Beil. XI-269, XI_1-(63)] with PCl_5 see (6); from 2-chloro-1-hydroxynaphthalenesulfonic acid-4 (1) by hydrolysis in boilg. dil. H_2SO_4 see (1).]

Č on stdg. in aq. Na_2CO_3 soln. gives blue flocks (7).

Č with 1 mole Br_2 in 20% AcOH yields alm. quant. (7) 4-bromo-2-chloro-naphthol-1, ndls., m.p. 112° (7).

[Č with conc. HI ($D = 1.5$) in boilg. AcOH for 12 hrs. reduces (4) to α-naphthol (1:1500), but Č is unaffected by $SnCl_2$ + HCl in alc. even after 28 hrs.' boilg. (4).]

[Č on oxidn. with p-diamines gives (3) indophenols; Č on coupling with diazonium salts gives (3) azo dyestuffs, cf. (1); Č with isatin chloride [Beil. XXI-302, XXI_1-(296)] yields (5) a chloronaphthalene indolindigo.]

[Č dislvd. in a little alc., made ammoniacal with conc. NH_4OH, and treated at 5° with nitrosobenzene in alc. gives (84% yield (8)) 2-chloronaphthoquinone-1,4-monoanil-4 (see under 3:3580), very red ndls. from alc., m.p. 112° (8).

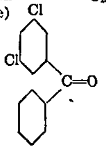
3:1490 (1) Hodgson, Rosenberg, *J. Soc. Chem. Ind.* **48-T**, 287–289 (1929). (2) Lesser, Gad, *Ber.* **56**, 972–973 (1923). (3) Kalle and Co., Ger. 167,458, Jan. 22, 1906; *Cent.* **1906**, I 1067. (4) Franzen, Steuble, *J. prakt. Chem.* (2) **103**, 383–384 (1921/2). (5) Bedzik, Friedländer, *Monatsh.* **29**, 380–381 (1908). (6) Claus, Oehler, *Ber.* **15**, 314 (1882). (7) Willstätter, Schuler, *Ber.* **61**, 365 Note, 367 (1928). (8) Friedländer, Sander, *Ber.* **57**, 646–647 (1924).

CHAPTER V

DIVISION A. SOLIDS

(3:1500–3:1999)

3:1505 3,5-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. S.N. 652
(3,5-Dichlorophenyl phenyl ketone)



M.P. 65° (1) (2)

Ndls. (from MeOH (1)).

[For prepn. from 3,5-dichloro-4-aminobenzophenone (1) by removal of amino group via diazo reaction see (1); for prepn. from 3,5-dichlorobenzohydrol by oxidn. with CrO_3 (75% yield) see (2).]

C̄ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (2) BzOH (1:0715) and a trace of *m*-dichlorobenzene (3:5960).

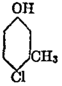
Ⓓ **3,5-Dichlorobenzophenone oxime:** from C̄ in alc. on refluxing 8 hrs. with $NH_2OH.HCl$ + excess NaOH: after distilling off the alcohol, the mixt. of two stereoisomeric oximes is pptd. by pouring into aq.; sepn. of the two isomers can be effected by fractnl. crystn. from dil. MeOH or dil. EtOH (1).

α-form (less-soluble isomer), pl or fine ndls., m.p. 137°. [With PCl_5 in dry ether, followed by water, this form yields quant. 3,5-dichlorobenzanilide, ndls. from dil. alc., m.p. 148° (1).]

β-form (more-soluble isomer), constituting 70% of reaction mixt, pr. m.p. 118°. [With PCl_5 in dry ether, followed by water, this form yields a gummy product from which some benz-3,5-dichloroanilide, ndls. m.p. 148 5°, can be sepd. (1).]

3:1505 (1) Waters, *J. Chem. Soc.* **1929**, 2108–2109. (2) Lock, Rödiger, *Ber.* **72**, 869–870 (1939).

3:1535 4-CHLORO-3-METHYLPHENOL C_7H_7OCl Beil. VI - 381
(4-Chloro-*m*-cresol) VI_1-(187)
VI_2-(355)



M.P. 66°	(1) (11)	B.P. 235°	(1)
57°	(2)	234–236°	(11)
55.5°	(3)		

Note that Č is often designated in the literature as "*p*-chloro-*m*-cresol" or even as "6-chloro-*m*-cresol"; care must be taken to avoid confusion with the isomeric 6-chloro-3-methylphenol (3:0700).

Odorless cryst. (from lgr.). — Volatile with steam (3).

Both the low-melting and high-melting forms appear to be authentic; whether they are different cryst. forms has never been detd.

[For prepn of Č from 2-chloro-5-aminotoluene (4-chloro-3-methylaniline) [Beil. XII-871] via diazo reaction see (3); for comml. prepn. from *m*-cresol (1:1730) by chlorination with SO_2Cl_2 see (1) (4) (84% yield (11)).]

[Č on monobromination with Br_2 in AcOH gives (8) 4-chloro-6-bromo-3-methylphenol, m p. 70.0–70.5° (8); Č on dibromination yields (9) 4-chloro-2,6-dibromo-3-methylphenol, m p 68 5–69.5° (9) (for use of latter in bromometric detn. of Č see (10)).]

Č treated with $(CH_3)_2SO_4$ + aq NaOH gives its methyl ether, 4-chloro-3-methylanisole, b p 213 5° (2). [This methyl ether on oxidn with dil. $KMnO_4$ (6 7 hrs. for 5 g.) gave (2) 2-chloro-5-methoxybenzoic ac [Beil. X-143], ndls. from dil AcOH (5), m.p. 173.5° (2), 170–171° (5), Neut. Eq. 186 5.

Ⓓ **4-Chloro-3-methylphenyl benzoate:** from Č + BzCl + pyridine, pl. from alc., m.p. 86° (2) (3). [This benzoate htd with 0.7 of its wt. of $AlCl_3$ for 10 min. at 140° gives by Fries rearrangement 100% yield (6) of 2-hydroxy-5-chloro-4-methylbenzophenone, yel. ndls. from dil. alc , m p. 142° (6)]

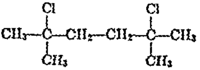
Ⓓ **4-Chloro-3-methylphenyl benzenesulfonate:** from Č + benzenesulfonyl chloride + pyridine, pl. from alc., m p. 66° (3). [Note that this value is numerically the same as orig Č and that the deriv must therefore be distinguished from it, e g , by mixed m p. or behavior with alk.]

Ⓓ **4-Chloro-3-methylphenyl *p*-toluenesulfonate:** from Č + *p*-toluenesulfonyl chloride + pyridine, pl from alc (2) (3), ndls from lt. pet (2), m p. 98° (2) (3). [Note that this deriv does not distinguish Č from 6-chloro-3-methylphenol (3:0700) or 2-chloro-3-methylphenol (3:1035).]

Ⓓ ***4-Chloro-3-methylphenyl N-α-naphthylcarbamate:* *from* Č + *α-naphthyl isocyanate*** in presence of trace of trimethyl- or triethyl-amine in ether; cryst from lgr., m.p. 153–154° (7).

3:1535 (1) Kalle and Co , Jan 11, 1897, Ger. 90,847, *Friedländer* **4**, 94 (1894/7). (2) Gibson, *J. Chem. Soc.* **1926**, 1425–1428. (3) Huston, Chen, *J. Am. Chem. Soc.* **55**, 4214–4218 (1933). (4) Laschinger, U.S. 1,847,566, March 1, 1932, *Cent* **1932**, II 1512, *C.A* **26**, 2471 (1932). (5) Hodgson, Beard, *J. Chem. Soc* **1926**, 154 (6) Rosenmund, Schnurr, *Ann.* **460**, 86 (1928). (7) French, Wirtel, *J. Am Chem Soc* **48**, 1736–1739 (1926). (8) von Walther, Zipper, *J. prakt. Chem.* (2) **91**, 378–379 (1915) (9) Huston, Neeley, *J Am. Chem. Soc.* **57**, 2178 (1935). (10) Deshusses, *Mitt. Lebensm. Hyg* **32**, 250–254 (1941); *C A.* **37**, 3023 (1943).
(11) Sah, Anderson, *J. Am Chem Soc.* **63**, 3165 (1941).

3:1550 2,5-DICHLORO-2,5-DIMETHYLHEXANE (Di-isocrotyl-*bis*-hydrochloride) $C_8H_{16}Cl_2$ **Beil. I - 163**, **I_1—**, **I_2-(127)**



M.P. 66–67° (1)
64° (2) (3)

Colorless lfts. or ndls., sol. in alc , ether, $CHCl_3$, or C_6H_6

[For prepn. of Č from 2,5-dimethylhexanediol-2,5 [Beil. I-492, I_1-(256), I_2-(557)] with

fumg. HCl (1) or AcCl (1) or in AcOH with HCl gas (100% yield (3)) see (1) (3); from the ring-closed internal ether of the above diol, viz., 2,2,5,5-tetramethyltetrahydrofuran [Beil. XVII-17], with fumg. HCl see (2); for prepn. of C̃ from 2,5-dimethylhexadiene-2,4 (di-isocrotyl) [Beil. I-259, I_1-(122), I_2-(237)] with HCl in s.t. see (2).]

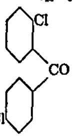
C̃ on htg. boils at 180° with evolution of HCl (1).

[C̃ on slow distn. at 12–20 mm. over CO_2 saturated soda-lime at 255–270° gives (3) by loss of 2 HCl 2,5-dimethylhexadiene-2,4 (see above), m.p. + 6° (2).]

[For study of behavior of C̃ with aq. alc. $N/10$ NaOH see (4).]

3:1550 (1) Henry, *Compt. rend.* **143**, 496–497 (1906). (2) Pogorzelski, *J. Russ. Phys.-Chem. Soc.* **30**, 977–992 (1898); *Cent.* **1899**, I 773. (3) Staudinger, Muntwyler, Ruzicka, Seibt, *Helv. Chim. Acta* **7**, 395–396 (1924). (4) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1380–1388 (1939); *C.A.* **34**, 1611 (1940).

3:1565 2,4′-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ **Beil. VII - 420**
(*o*-Chlorophenyl *p*-chlorophenyl ketone) **VII_1—**



M.P. 66.5–67.0°	**(1) (2)**	**B.P. 214–215° at 22 mm.**	**(2)**
66°	**(3) (4)**		
64.2–65.2° cor.	**(5)**		

Pr. (from alc.). — [For crystallographic consts. see (3) (4).] — Sol. in most org. solv.; cryst. best from lgr. or cold dil. (60–75%) alc. (2).

[For prepn. from *o*-chlorobenzoyl chloride (3:6640) + chlorobenzene (3:7903) + $AlCl_3$ in CS_2 see (2); as by-product (besides 4,4′-dichlorobenzophenone (3:4270)) from *p*-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) + $AlCl_3$ + CS_2 see (3), or from *p*-chlorobenzoic acid (3:4940) + chlorobenzene (3:7903) + $AlCl_3$ (yield 9–12%) see (1).]

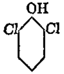
[For formn. of C̃ from 1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:1925) by oxidn. with CrO_3/AcOH see (5).]

[C̃ with aq. NaOH + trace CuO in Fe bomb (or in pres. of Fe powder) at 240° for 6 hrs. both ring-closes and hydrolyzes giving (87% yield (6)) crude 3-hydroxyfluorenone, m.p. 184–192° (6).]

Ⓓ **2,4′-Dichlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 230–231° (5).

3:1565 (1) Newton, Groggins, *Ind. Eng. Chem.* **27**, 1399 (1935). (2) Norris, Twieg, *Am. Chem. J.* **30**, 397 (1903). (3) Montagne, *Rec. trav. chim.* **25**, 385–387 (1906). (4) Jaeger, *Z. Krist.* **56**, 52 (1921). (5) Haller, Bartlett, Drake, Newman, Cristol, Magerlein, Mueller, Schneider, *J. Am. Chem. Soc.* **67**, 1599, 1602 (1945). (6) Britton, Moyle, Bryner (to Dow Chem. Co.), U.S. 2,377,751, June 5, 1945; *C.A.* **39**, 4097 (1945).

3:1595 2,6-DICHLOROPHENOL $C_6H_4OCl_2$ **Beil. VI - 190**
VI_1-(103)
VI_2-(179)



M.P. 67°	**(1) (2)**	**B.P. 219–220°**	at 740 mm.	(2) cf. (3)
66–68°	**(8)**	**80–85°**	at 4 mm.	(2)

Cryst. from pet. eth. with penetrating odor suggesting o-chlorophenol or (if dilute) iodoform. — Misc. with alc., ether, volatile with steam.

[For prepn. from p-hydroxybenzoic ac (1:0840) by chlorination in AcOH followed by elimin. of CO_2 by htg in quinoline see (4) (5) (8); for prepn. from phenol (1:1420) by *prelim. sulfonation*, subsequent chlorination in nitrobenzene, and final removal of sulfonic acid group by hydrolysis (70% yield (2)) see (2).]

C̄ is sol. in Na_2CO_3 soln. (1). [For study of ionization const. see (6).]

C̄ on nitration (no details) gives 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., m.p. 125° (7).

C̄ dislvd. in aq. alk. and shaken with $(CH_3)_2SO_4$ yields (1) (2) the methyl ether, 2,6-dichloroanisole, b.p. *105–106° at 20 mm* (2), m.p. 10 1° (1).

[For study of rearr. of ethers (8) or esters (9) of C̄ see indic. refs.]

—— **2,6-Dichlorophenyl acetate:** b.p. 125–126° at 17 mm., D_{25}^{25} = 1.335, n_D^{23} = 1.5281 (8). [From C̄ with Ac_2O + pyridine (93% yield (8)).]

Ⓓ **2,6-Dichlorophenyl benzoate:** m.p. 74.0–74.5° (9).

—— **2,6-Dichlorophenyl p-nitrobenzoate:** unreported.

—— **2,6-Dichlorophenyl 3,5-dinitrobenzoate:** unreported.

—— **2,6-Dichlorophenyl benzyl ether:** m.p. 39.5–40° (10).

—— **2,6-Dichlorophenyl p-nitrobenzyl ether:** unreported.

Ⓓ **2,6-Dichlorophenoxyacetic acid:** ndls. from aq., m.p. 134 5–135.0° cor. (9). [From C̄ with chloroacetic acid (3:1370) + aq. alk. (9).]

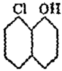
—— **2,6-Dichlorophenyl N-phenylcarbamate:** unreported.

—— **2,6-Dichlorophenyl N-(α-naphthyl)carbamate:** unreported.

—— **2,6-Dichlorophenyl N-(β-naphthyl)carbamate:** unreported.

3:1595 (1) Holleman, *Rec. trav. chim.* **37**, 96–103 (1918). (2) Huston, Neeley, *J. Am. Chem. Soc.* **57**, 2177 (1935). (3) Seifart, *Ann. Suppl.* **7**, 203 (1870). (4) Richardson, *J. Chem. Soc.* **1937**, 1364. (5) Blicke, Smith, Powers, *J. Am. Chem. Soc.* **54**, 1468 (1932). (6) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935). (7) Tarugi, *Gazz. chim. ital.* **30**, II 490–491 (1900). (8) Tarbell, Wilson, *J. Am. Chem. Soc.* **64**, 1068–1069 (1942). (9) Tarbell, Fanta, *J. Am. Chem. Soc.* **65**, 2172–2173 (1943). (10) Huston, Eldridge, *J. Am. Chem. Soc.* **53**, 2262–2263 (1931).

3:1610 8-CHLORONAPHTHOL-1



$C_{10}H_7OCl$ Beil. VI — VI_1— VI_2-(582)

M.P. 67° (1)

Ndls. from aq. — Volatile with steam.

[For formn. of C̄ from *8-chloro-1-nitronaphthalene* [Beil. V-556] by merely refluxing with aq. see (1).]

C̄ is sol. in aq. alk. giving orange-colored soln. which couples with solns. of diazonium salts (1).

[For reactn. of C̄ with benzotrichloride (3:6540) yielding 4-benzoyl-8-chloronaphthol-1, m.p. 121°, used in prepn. of triphenylmethane dyes see (2); with o-nitrophenylsulfenyl chloride see (3); *for coupling of C̄ with diazotized 2-hydroxynaphthylamine-1 (or its relatives)* yielding o-hydroxyazo cpds. see (4).]

3:1610 (1) Woroshtzow, Koslow, *Ber.* **69**, 412–415 (1936). (2) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923. Ger. 378,909, Aug. 11, 1923; Swiss 98,559, April 2, 1923; *Cent.* **1923**, IV 694. (3) Akt.-Ges. Anilin-Fabrikation, Ger. 402,642; Sept. 17, 1924; *Cent.* **1924**, *II 2505*. (4) Soc. Chem. Ind. Basel, Brit. 180,433, June 22, 1922; *Cent.* **1922**, IV 841.

3:1615 α-CHLOROISOCROTONIC ACID (*cis*-2-Chlorobuten-2-oic acid-1; *allo*-α-chlorocrotonic acid)

$CH_3—C—H$
$\quad\quad\|$
$HOOC—C—Cl$

$C_4H_5O_2Cl$

Beil. II - 415
II_1-(189)
II_2-(396)

M.P. 67.0–67.5° (1)
66–67° (2)
67° (3)
66.2–66.5° (4) (5)
66° (6) (7)

[*See also α-chlorocrotonic acid* (3:2760).]

Ndls. from aq. (2) (4) (5); note, however, that from aq. solns. of salts acidification first ppts. C̄ as an oil. — C̄ is more sol. aq. than its stereoisomer; e.g., C̄ is sol. in 15.3 pts. aq. at 19° (8). — C̄ is much more volatile with steam than its stereoisomer (3:2760) (4) (5). — C̄ is spar. sol. cold but eas. sol. hot lgr. (8).

Preparation. [For prepn. of C̄ from lower-melting form (m.p. 63°) of α,β-dichloro-*n*-butyric acid (3:1375) with excess 10% aq. NaOH at not above 10° see (4) (5) cf. (9).]

Chemical behavior. C̄ on htg. in s.t. at 150–160° for 12 hrs. (10), or with pyridine hydrochloride in pyridine 7 days at room temp. or rapidly at 100° (2), or even slowly on steam distillation (11) is converted to the stereoisomeric α-chlorocrotonic acid (3:2760), m.p. 99°.

C̄ on reduction with Na/Hg in aq. is dehalogenated yielding (12) (4) crotonic acid (1:0425), m.p. 72°; whether any isocrotonic acid (1:1045), b p. 169°, m.p. 15°, is formed at all is uncertain.

C̄ with Cl_2 in CS_2 adds 1 mole halogen yielding (13) the same α,α,β-trichloro-*n*-butyric acid (3:1280), m.p. 59.5–60°, also obtd. by like treatment of α-chlorocrotonic acid (3:2760). — The behavior of C̄ with Br_2 appears to be unreported.

C̄ behaves as a monobasic acid; dissociation const. at 25° is 1.58×10^{-3} (14); Neut. Eq. 120.5.

Salts. [KĀ, ndls. from alc. in which it is much more sol. (viz., 1 pt. KĀ in 22 pts. 99.5% alc. at 16.5° (4)) than its stereoisomer (use in sepn. (2) (9)), eas. sol. aq.; $BaĀ_2$ $3\frac{1}{2}H_2O$, eas. sol. aq. but spar. sol. alc. (8); $PbĀ_2.H_2O$, ppt. (8).]

[*For study of rate of reactn. of C̄ with K_3AsO_3 see (3).*]

The acid chloride of C̄ is unreported.

—— **Methyl α-chloroisocrotonate:** unreported. [*However, for study of rate of esterification of C̄ with MeOH see (15).*]

—— **Ethyl α-chloroisocrotonate:** oil; see 3:9368. [Note also that C̄ in EtOH with conc. H_2SO_4 at 100° gives only (7) the stereoisomeric ethyl α-chlorocrotonate (3:8523).]

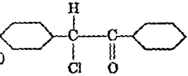
—— **α-Chloroisocrotonamide:** unreported.

—— **α-Chloroisocrotonanilide:** unreported.

—— **α-Chloroisocroton-α-naphthalide:** unreported.

3:1615 (1) Stelling, *Z. physik. Chem* ... (3)
Backer, van Oosten, *Rec. trav. chim.* E
(5) Wislicenus, *Ber.* 20, 1008–1010 (18
Ann. **432**, 62 (1923). (8) Michael,
thess, *J. prakt. Chem.* (2) **46**, 255–2
38, 4 (1888).
(11) Wislicenus, *Ann.* **248**, 337 (1888). (12) Michael, *J. prakt. Chem.* (2) **46**, 270–272 (1892). (13) Valentin, *Ber.* **28**, 2661–2662 (1895). (14) Ostwald, *Z. physik. Chem.* **3**, 244 (1889). (15) Michael, Oechslin, *Ber.* **42**, 322 (1909).

3:1618 *d,l*-DESYL CHLORIDE $C_{14}H_{11}OCl$ Beil. VII - 436
(α-Chlorodesoxybenzoin, VII_1-(234)
ms-chlorodesoxybenzoin,
α-chlorobenzyl phenyl ketone,
α-chloro-α-phenyl-acetophenone)



M.P.	68°	(1) cf. (2)
	67.5°	(3) (4)
	67.0–67.5°	(5)
	67°	(6)
	66–68°	(7)
	66–67°	(8) (9)
	66°	(2)
	65.5°	(10)
	65°	(11) (12)

White cryst. from MeOH, EtOH, lgr., or $CHCl_3$ by addn. of lt. pet. — Note that on distillation under reduced press. C̄ goes over with only slight decompn. as a green vapor which condenses to a green liquid, on solidification much of this color is lost and recrystallization yields colorless C̄. — C̄ is quite stable in dark; in sunlight, however, it turns brown and decomposes.

PREPARATION OF C̄

[For prepn. of C̄ from benzoin (1:5210) with $SOCl_2$ in pyridine (yield 74–79% (9)) (5) or with $SOCl_2$ directly (yield 90% (6)) (2) (3) (10) (13) see indic. refs. — Note that *l*-benzoin with $SOCl_2$ undergoes racemization (7) yielding C̄.]

[For formn of C̄ from α,α-dichlorobenzyl phenyl ketone (*ms,ms*-dichlorodesoxybenzoin) [Beil. VII-436, VII_1-(234)] by partial dehalogenative reduction using H_2 + platinum oxide cat. (65% yield (1)) or AcOH + Fe powder at 70–80° (15) see indic. refs.; from 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene) with conc. HCl in s.t. at 120° for 2 hrs. see (11); from benzoyl-phenyl-diazomethane (azibenzil) [Beil. VII_1-(395)] in ether with HCl gas see (12).]

CHEMICAL BEHAVIOR OF C̄ WITH INORGANIC REAGENTS

Reduction. [C̄ in alc. soln. with H_2 + platinum oxide cat. (1), or in AcOH with Fe powder on protracted treatment (14), gives benzyl phenyl ketone (desoxybenzoin) (1:5165).]

Oxidation. [C̄ with conc. HNO_3 on warming gives (14) dibenzoyl (benzil) (1:9015).]

Halogenation. [C̄ with Br_2 (1 mole) in AcOH at 100° for ½ hr. gives (10) α-bromo-α-chlorobenzyl phenyl ketone, m.p. 85°.]

Behavior with alkalies and alkali carbonates. (For alc. alkalies see below under organic reactants.) — [C̄ with powdered KOH (3 moles) in toluene refluxed 2 hrs. loses HCl and rearranges giving (20% yield (11)) 1,2-diphenyl-1,2-epoxyethylene (diphenyloxene), b.p. 174–180° at 18 mm., m.p. 52°; note, however, that two later workers (15) (29) have been unable to duplicate this report. — Note, however, that C̄ with powdered KOH in dry ether gives (15) a mixt. of benzoic acid (1:0715), diphenylacetic acid (1:0765), desoxybenzoin (1:5165), and benzil (1:9015).]

[C̄ with excess ignited Na_2CO_3 at 200° without solvent for 1 hr. gives (11) a mixt. (yield not stated) of both stereoisomeric 1,2-dibenzoyl-1,2-diphenylethylenes (dibenzoylstilbenes): higher-melting isomer [Beil. VII-844], m.p. 232°; lower-melting isomer [Beil. VII-843, VII_1-(453)], m.p. 212–214°.]

[$\bar{C}$ with NaSH in alc. soln. in cold gives (16) benzoyl-phenyl-carbinyl mercaptan (desylthiol), m.p. 42–44° (benzoyl ester, m.p. 110–112° (16)), accompanied by two forms of didesyl sulfide, one of m.p. 168–169°, the other of m.p. 128–129° (16).]

Behavior with metals. [$\bar{C}$ with Na in C_6H_6 evolves H_2 and on warming gives a mixt. which with aq. followed by dil. acid gives (2) a mixt. of benzoic acid (1:0715) + benzilic acid (1:0770) together with an unidentified neutral oil.]

Behavior with other inorganic reactants. [$\bar{C}$ with moist silver oxide in ethylene glycol at 100° for 3 hrs., then boiled 2 hrs., gives (29) 1,2-dibenzoyl-1,2-diphenylethane (bidesyl) [Beil. VII-841, VII_1-(452)], m.p. 254–255° (29).]

CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

Behavior with arom. hydrocarbons + $AlCl_3$. [$\bar{C}$ with C_6H_6 (1:7400) + $AlCl_3$ gives (78% yield (17)) (18) (19) ω,ω-diphenylacetophenone (*ms*-phenyldesoxybenzoin = triphenylvinyl alc.) [Beil. VII-522, VII_1-(291)], m.p. 137° (19), 135–136° (17) (18). — $\bar{C}$ with toluene (1:7405) + $AlCl_3$ gives (77% yield (17)) ω-phenyl-ω-(*p*-tolyl)acetophenone (α-(*p*-tolyl)-desoxybenzoin), m.p. 97–98° (17). — $\bar{C}$ with mesitylene (1:7455) + $AlCl_3$ in CS_2 gives (13) ω-phenyl-ω-mesitylacetophenone (α-mesityldesoxybenzoin), m.p. 111–112° (13).] (See also below under reactn. of $\bar{C}$ with RMgX cpds.)

Behavior with organic hydroxy or mercapto compounds. *With alcohols (or alkoxides).* [$\bar{C}$ in MeOH with MeOH/NaOMe gives (80% yield (11)) 1,2-diphenyl-1-methoxy-1,2-epoxyethane, b.p. 194–196° at 16 mm., accompanied by some *cis* + *trans* dibenzoylstilbene (see above).]

[$\bar{C}$ in EtOH with EtOH/NaOEt gives similarly a prod., b.p. 188° at 12 mm., regarded (11) as 1,2-diphenyl-1-ethoxy-1,2-epoxypropane. — Note, however, that $\bar{C}$ in EtOH/NaOEt or with alc. NaOH at 25° gives (5) cf. (1) benzoin (1:5210) and that under certain conditions an apparently intermediate benzoin diethylacetal $C_6H_5CH(OH).C(OC_2H_5)_2.C_6H_5$, m.p. 66–67°, can be isolated (5).]

With phenols (or alkali phenates). [$\bar{C}$ with phenol + anhydrous K_2CO_3 in acetone refluxed 5 hrs. (20) or $\bar{C}$ with Na phenate (21) gives (59% yield (20)) desyl phenyl ether (the phenyl ether of benzoin), m.p. 85.5° (21), 85° (20); note that this prod. is isomeric with, but different from, *ms*-phenylbenzoin [Beil. VIII–211], whose m.p. is almost the same; note also that desyl phenyl ether on attempted distillation at ord. press. undergoes a fission into phenol and a cpd. regarded (21) as 2,2,4,4-tetraphenylcyclobutanedione-1,3, m.p. 244–245°.]

With mercaptans. [$\bar{C}$ + α-mercaptoacetic acid (thioglycolic acid) at 100° for 6 hrs. evolves HCl and yields (22) *S*-desylthioglycolic acid, m.p. 105° (corresp. oxime, m.p. 123°; corresp. semicarbazone, m.p. 178° (22)). — $\bar{C}$ with β-mercaptopropionic acid at 100° for 6 hrs. evolves HCl and yields (16) β-(desylthio)propionic acid, m.p. 108–109°.]

[$\bar{C}$ with thiophenol in EtOH/NaOEt gives in good yield (16) desyl phenyl sulfide, m.p. 83–84° (16), 81° (23). — $\bar{C}$ in MeOH with aq. sodium thiosalicylate gives (22) *S*-desylthiosalicylic acid, m.p. 189°.]

Behavior with carbonyl compounds. [For behavior of $\bar{C}$ with cyclohexanone + sodium in di-*n*-butyl ether see (24).]

Behavior with organic acids (or their salts). [$\bar{C}$ with anhydrous NaOAc in excess Ac_2O refluxed 1 hr. yields (11) mainly the β-stereoisomer, m.p. 153°, of 1,2-diacetoxy-1,2-diphenylethylene [Beil. VI-1026, VI_1-(499)], accompanied by some of the more sol. α-stereoisomer, m.p. 118°.]

[$\bar{C}$ + K thiobenzoate in abs. alc. boiled 10 min. gives (100% yield (16)) desyl thiobenzoate, m.p. 110–112°.]

[$\bar{C}$ in aq. alc. KCN does *not* directly eliminate KCl and give the corresp. desyl cyanide

(*ms*-cyanodesoxybenzoin) [Beil. X-755, X_1-(360)] which might be expected although this compd., m p. 90–92° (25), 89–90° (26), is well known and preparable (yields 60% (25), 47% (26)) from benzyl cyanide + ethyl benzoate and otherwise. — Instead C̄ in aq. alc. KCN loses HCl and gives (27) (28) 1-cyano-1,2-diphenyl-1,2-epoxyethane (α-cyano-α,β-diphenyl-ethylene oxide) which obviously can exist in two geometrically stereoisomeric forms: one has m p 74° (27), 77–78° (28); the other has m.p. 52° (27); for much further detail especially with reference to further reactn prods of these epoxynitriles see (27) (28)]

Behavior of C̄ with RMgBr reactants. (See also above under behavior of C̄ with hydrocarbons + $AlCl_3$.)

[C̄ with C_6H_5MgBr (2 moles) gives (29) (21) the prod. normally to be expected, viz., 1,1,2,2-tetraphenylethanol-1 [Beil VI-732, VI_1-(364)], m p. 236° (21) (30), 230 5° (29); the intermediate ketone, viz., *ms*-phenyldesoxybenzoin (for consts. see above reference) may sometimes (21) be formed, but for discussion of possible alternative mechanisms see (21) (29)]

C̄ with the three tolyl MgBr reactants has been studied, but the reaction is complex and shows no tendency to go way through to the expected tetraarylethanols (only one of which has been reported by any means). — [C̄ with *o*-tolyl MgBr (2 moles) gives (29) a mixt. of prods., including the expected intermediate ketone, viz , *ms*-(*o*-tolyl)desoxybenzoin, m p. 56–57° (32); note, however, that the 1,2-diphenyl-1,2-di-(*o*-tolyl)ethanol-1 which should be the end prod is unknown. — C̄ with *m*-tolyl MgBr gives (29) similarly a mixt. of prods. including the intermediate ketone, viz., *ms*-(*m*-tolyl)desoxybenzoin, m.p 83–84° (32), 82.5–83.5° (29), 82–83° (33), but again the ultimate 1,2-diphenyl-1,2-di-(*m*-tolyl)-ethanol-1 is unknown. — C̄ with *p*-tolyl MgBr (2 moles) gives (31) the ketone *ms*-(*p*-tolyl)desoxybenzoin, m.p. 97–98° (17), 96–97° (31); the ultimate 1,1-diphenyl-1,2-di-(*p*-tolyl)ethanol-1, m.p. 195–196°, has been obtd. by other means (29)]

Behavior of C̄ with amines. *With primary amines* [C̄ (1 mole) with aniline (2 moles) in alc. at room temp. for 24 hrs gives (6) *N*-(desyl)aniline (benzoin anil = *ms*-anilinodesoxybenzoin) [Beil. XIV-103, XIV_1-(395)], m p 99°; note that C̄ with aniline at 140–150° for 1hr. (34) ppts. aniline hydrochloride and leaves a mixt. contg. benzoin-anil = anilide (cf. (35)) since with benzaldehyde at 150–160° for 1 hr. under CO_2 it yields pentaphenyldihydroimidazole (31) — C̄ with p-toluidine in alc at room temp. for 24 hrs gives (3) similarly *N*-(desyl)-*p*-toluidine (*ms*-(*p*-toluidino)desoxybenzoin), m p. 145°]

[For corresp. reactns. of C̄ with *m*-chloroaniline, *p*-chloroaniline, *m*-bromoaniline, *p*-iodoaniline, *p*-aminophenol, *p*-phenetidine, *p*-aminoacetanilide, or ethyl *p*-aminobenzoate see (3), for study of rate of this group of reactns see (4); note that *o*-toluidine, *o*-chloroaniline, and *o*-anisidine do *not* undergo this reactn. (3).]

With secondary amines. [C̄ with Me_2NH (2–3 moles) in alc. in s.t. at 100–110° gives (36) *ms*-(dimethylamino)desoxybenzoin, m.p. 59–61° (36).]

[C̄ (1 mole) with *N*-methylaniline (2 moles) in alc. refluxed 2½ hrs. gives (47% yield (3)) *ms*-(*N*-methyl-*N*-phenylamino)desoxybenzoin, m.p. 100°; if reactants in alc. are stood at room temp. for 100 days, yield is 61% (3).]

[C̄ with piperidine at 100° for 20 min. gives (8) *ms*-(piperidino)desoxybenzoin [Beil. XX_1-(14)], m p. 85–86° (8).]

With phenylhydrazine C̄ (1 mole) with phenylhydrazine (2 moles) in abs alc. at room temp. for 3 days ppts. phenylhydrazine hydrochloride and yields (37) benzil *bis*-(phenylhydrazone) = benzil-phenylosazone, m.p. 233° dec. (37) [cf. under benzil (1:9015)]

Ⓓ *N*-Desylphthalimide [Beil. XXI-480, XXI_1-(374)]: pale yel. cryst. from AcOH. m p. 157–158° (38), 155–156° (39). [From C̄ with K phthalimide at 100° for 2 hrs, (21% yield (39)); note that C̄ + potassium phthalimide in nitrobenzene at 150–160°

for 1½ hrs. gives a mixt. of *N*-desylphthalimide with the lower-melting stereoisomer of dibenzoylstilbene (1,2-dibenzoyl-1,2-diphenylethylene) [Beil. VII-843, VII_1-(453)], m.p. 208° (39) (see also above).]

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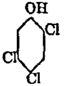
(21) Richard, *Compt. rend.* **198**, 1242–1244 (1934). (22) Behaghel, Schneider, *Ber.* **68**, 1590, 1593 (1935). (23) Mitchell, Smiles, *J. Chem. Soc.* **1933**, 1529. (24) Allen, *Can. J. Research* **4**, 271–272 (1931). (25) Kohler, Blatt, *J. Am. Chem. Soc.* **50**, 507–508 (1928). (26) Howk, McElvain, *J. Am. Chem. Soc.* **54**, 286 (1932). (27) Kohler, Brown, *J. Am. Chem. Soc.* **55**, 4299–4304 (1933). (28) Richard, *Compt. rend.* **198**, 943–945 (1934). (29) Roger, McGregor, *J. Chem. Soc.* **1934**, 1850–1853. (30) Wegler, *Ber.* **67**, 35–39 (1934).

(31) McKenzie, Roger, McKay, *J. Chem. Soc.* **1932**, 2603. (32) Roger, McKay, *J. Chem. Soc.* **1933**, 336. (33) Roger, McGregor, *J. Chem. Soc.* **1932**, 443. (34) Langenbeck, Hutschenreuter, Jüttemann, *Ann.* **485**, 54, 57–58 (1931). (35) Strain, *J. Am. Chem. Soc.* **50**, 2221 (1928). (36) Thomson, Stevens, *J. Chem. Soc.* **1932**, 1937. (37) Bodforss, *Ber.* **71**, 481 (1939). (38) Neumann, *Ber.* **23**, 995 (1890). (39) McKenzie, Barrow, *J. Chem. Soc.* **103**, 1333 (1913).

3:1620 2,4,5-TRICHLOROPHENOL



$C_6H_3OCl_3$ Beil. VI — VI_1— VI_2-(180)

M.P. 68°	(1) (2)	B.P. 244–248° at 746 mm. (5) (9)
67.5°	(3)	
66–67°	(4)	
66°	(5) (6) (7)	
64–65°	(8)	
63°	(9)	

Colorless ndls. from alc. or lgr. — Volatile with steam. — Sublimes.

[For prepn. of C̄ from 1,2,4,5-tetrachlorobenzene (3:4115) with MeOH/NaOH in s.t. at 160° for 7 hrs. (yields: 85% (5), 80% (10)) (note that by this method C̄ is sometimes sole product (5), at others is accompanied (7) (10) by some of its methyl ether (2,4,5-trichloroanisole) (see below)) see indic. refs.; from 2,4,5-trichloroaniline via diazotization in conc. H_2SO_4 as directed followed by htg. at 170–180° (65% yield (9)) see indic. refs.; from 2,4,5-trichloro-1-fluorobenzene with NaOMe see (6); from 3,5,6-trichloro-2-hydroxybenzoic acid by htg. with soda-lime at 185° see (3); from 2,4-dichloro-5-aminophenyl *o*-amino-*p*-toluenesulfonate via diazotization, use of Cu_2Cl_2 reactn., and subsequent hydrolysis as directed see (4); from 2,5-dichlorophenol (3:1190) with Cl_2 in AcOH (9) or in AcOH + NaOAc (4) see indic. refs.]

C̄ behaves as a weak monobasic acid (ioniz. const. at 25° = 4.3×10^{-8} (2)) but can be titrated with *N*/10 aq. NaOH; Neut. Eq. calcd. 197.5, found 197.1 (1). — C̄ forms a spar.

sol. K salt (4). — C̄ in toluene treated with MeOH/NaOH yields (11) anhydrous Na salt; from aq. this prod. cryst. as pentahydrate (12). — [For prepn. of Na, K, or Li salts see (12), of Ca or Ba salts see (13), of Zn salt see (14). — For use of these salts as fungicides see (11) (12) (13) (14) (15); for use of C̄ with triphenyl phosphate as wood preservative see (16).]

C̄ with Br_2 in AcOH (9) or with excess Br_2/aq (17) yields 6-bromo-2,4,5-trichlorophenol, cryst from AcOH or lt. pet., m p 81–82° (17), 81° (9) (corresp. benzoate, m.p. 116–117° (9)). — C̄ with Br_2 in pres. of Fe powder yields (9) 3,6-dibromo-2,4,5-trichlorophenol, ndls from AcOH, m p. 195° (9) (corresp. benzoate, m.p. 176° (9)).

C̄ treated below 10° with conc. HNO_3 ($D = 1.43$) in AcOH gives (90% yield (5)) 6-*nitro-2,4,5-trichlorophenol*, *pale yel. lfts.* from lgr., m.p. 92–93° (5), 81° (9).

C̄ dslvd in 20% NaOH refluxed with Me_2SO_4 gives (78.5% yield (5)) (9) corresp. methyl ether (2,4,5-trichloroanisole), ndls from alc., m.p. 75° (5), 77.5° (9).

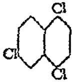
Ⓓ **2,4,5-Trichlorophenyl benzoate:** ndls. from alc., m.p. 92–93° (9), 91–92° (4), 89–90° (3). [From C̄ in dil. alk. by shaking with benzoyl chloride (9).]

Ⓓ ***2,4,5-Trichlorophenoxyacetic acid:*** *m p. 153°* (see 3:4335).

3:1620 (1) Tiessens, *Rec. trav chim.* **50**, 114 (1931). (2) Tiessens, *Rec. trav. chim* **48**, 1068 (1929). (3) Farinholt, Stuart, Twiss, *J. Am chem Soc* **62**, 1240 (1940). (4) Groves, Turner, Sharp, *J. Chem. Soc.* **1929**, 516–517. (5) Harrison, Peters, Rowe, *J. Chem. Soc.* **1943**, 235–237. (6) de Crauw, *Rec. trav. chim* **48**, 1064–1065 (1929) (7) Holleman, *Rec. trav. chim.* **39**, 736–738 (1920). (8) A.G.F.A., Ger. 349,794, March 9, 1922, *Cent.* **1922**, IV 45 (9) Kohn, Fink, *Monatsh* **58**, 83–86 (1931) (10) A.G.F.A., Ger. 411,052, March 23, 1925, *Cent* **1925**, I 2411.

(11) Mills (to Dow Chem Co), U S. 1,955,080, April 17, 1934, *Cent* **1934**, II 1991. (12) Mills (to Dow Chem Co), U S. 1,991,329, Feb. 12, 1935, *Cent.* **1935**, II 2130 (13) Mills (to Dow Chem Co), U.S. 2,039,434, May 5, 1936, *Cent.* **1937**, I 984. (14) Mills (to Dow Chem. Co), U.S 1,994,002, March 12, 1935, *Cent.* **1935**, II 2431 (15) Ellis (to Insulite Co.), U.S. 2,161,654, June 6, 1939, *Cent* **1939**, II 4620 (16) Norton (to Dow Chem. Co), U.S. 2,301,013, Dec. 1, 1942, *C.A.* **37**, 2908 (1943). (17) Fox, Turner, *J. Chem. Soc.* **1930**, 1863.

3:1625 1,4,6-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V - 546
V_1—
V_2—

M.P. 69° (4)
68° (1)
65° (2) (3) (5) (7)
58° (1)
56° (2) (3) (7) (8) see text

Ndls. from alc.; spar. sol. boilg. alc. (2). — Volatile with steam. — Sublimes.

C̄ shows the double m.p. phenomena also exhibited by several of its isomers; if the fused C̄ in a m p. tube is allowed to cool and then withdrawn from the bath it soon solidifies to a translucent mass which upon immediate reimmersion melts at 58°, but if left for a short time in the air it becomes opaque and then shows m p. 68°; the translucent form rarely persists more than 20 min. (1).

[For prepn of C̄ from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] via diazotization and use of Cu_2Cl_2 reactn. see (4); for prepn. of C̄ from 1,6-dichloro-4-nitronaphthalene [Beil. V-556] (5) (2), from 4,6-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (6), from 4,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-163] (7), from 1,4-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (8) (6), from 1-chloro-4-nitronaphthalene-

$\bar{C}$ is readily nitrated; e.g., $\bar{C}$ (16 g.) dislvd. in a soln. of $NaNO_3$ (12 g.) in aq. (180 ml.), treated during 1 hr. at 90–100° by grad. addn. of dil. H_2SO_4 (1:5; 48 ml.), htd. 2 hrs. then steam-distd., gave (3) in distillate 3,5-dichloro-2-nitrophenol (5 g.), lemon-yel. ndls. from pet. ether m.p. 51°, and by repeated hot dil. HCl extraction of tarry residue 3,5-dichloro-4-nitrophenol (6 g.) pale yel. ndls. from aq., m.p. 150° (3). [This latter product also results from the action of nitrous acid (3).]

$\bar{C}$ dislvd. in 4 pts. AcOH and treated with 3 pts. fumg. HNO_3 for ¾ hr. at 70° (2) gives (60% yield (2)) of 3,5-dichloro-2,4,6-trinitrophenol, pale yel. pr. from AcOH, m.p. 139–140° cor. (2).

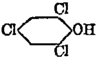
$\bar{C}$ dislvd. in 5 pts. AcOH gives with Br_2 (as specified (4)) 100% yield of 3,5-dichloro-2,4,6-tribromophenol, cryst. from AcOH, m.p. 189° (4).

$\bar{C}$ dislvd. in aq. NaOH and shaken with $(CH_3)_2SO_4$ gives the methyl ether, 3,5-dichloroanisole, m.p. 39° (6). [The value of 68° given in Ref. 6, p. 104, is probably erroneous.]

Ⓓ **3,5-Dichlorophenyl acetate:** m.p. 38° (5).
Ⓓ **3,5-Dichlorophenyl benzoate:** m.p. 55° (5).

3:1670 (1) Blanksma, *Rec. trav. chim.* **27**, 29–30 (1908). (2) Willstätter, Schudel, *Ber.* **51**, 784–787 (1918). (3) Hodgson, Wignall, *J. Chem. Soc.* **1927**, 2217–2218. (4) Kohn, Pfeifer, *Monatsh.* **48**, 237–239 (1927). (5) Hodgson, Wignall, *J. Chem. Soc.* **1926**, 2077–2079. (6) Holleman, *Rec. trav. chim.* **37**, 103–107, 201 (1918). (7) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935).

3:1673 2,4,6-TRICHLOROPHENOL



$C_6H_3OCl_3$ Beil. VI - 190
VI_1-(103)
VI_2-(181)

M.P.	69.5°	(1)	B.P.	246° at 760 mm.	(1)
	69° u.c.	(2)		245°	(8)
	69°	(3) (4)		243.5–244.5°	(12)
	68°	(5) (6) (7) (8)		242–246° at 748 mm.	(9)
	67–68°	(9) (10) (11) (12) (23)			
	67.0°	(13)			
	67°	(14)			
	66.7°	(15)			
	66–67° cor.	(16)			

Colorless cryst. from lgr. — Ndls. with 1 mole solvate from AcOH, latter lost over CaO (17).

$\bar{C}$ is almost insol. aq.: 1000 g. aq. at 11.2° dis. 0.51 g. $\bar{C}$ (14); at 25.4°, 0.858 g. $\bar{C}$ (14); at 96°, 2.43 g. $\bar{C}$ (14). — $\bar{C}$ is volatile with steam, but not from alk. soln. (difference and sepn. from *o*-chlorophenol (3:5980) or *p*-chlorophenol (3:0475) (18)). — $\bar{C}$ is eas. sol. alc. or ether.

Binary systems contg. $\bar{C}$. — $\bar{C}$ + *nitrobenzene:* this system forms a 1:1 molecular compound, m.p. 31°; this compd. forms with $\bar{C}$ a eutectic, m.p. 28.7° contg. 65 wt. % $\bar{C}$, and with nitrobenzene a eutectic, m.p. + 2.0° contg. 15.5 wt. % $\bar{C}$; for data and f.p./compn. diagram see (13). — $\bar{C}$ + *diphenylamine:* for partial f.p./compn. data and diag. see (19). — $\bar{C}$ + *2,4,6-tribromophenol:* for f.p./compn. data and diag. see (20). — $\bar{C}$ + *α,α,α,α'-tetramethylphthalan:* for study of this system see (15). — $\bar{C}$ + *2,4,6-trinitroresorcinol* (styphnic acid): forms no mol. cpd. but gives a eutectic, m.p. 60° contg. 91.8% $\bar{C}$ (21).

PREPARATION OF C̄

From phenol. *By direct action of chlorine.* [For prepn. of C̄ from phenol (1:1420) with Cl_2 see (3) (for very old initial work cf. (22) (12)); with Cl_2 + aq. alk. (i.e., with NaOCl) see (23) (16) (24).]

By indirect action of chlorine. [For prepn. of C̄ from phenol (1:1420) by chlorination with ethyl *N,N*-dichlorocarbamate (25), with *N,N'*-dichlorourea (26), with conc. HCl + 30% H_2O_2 (27), or with HCl + $KClO_3$ (28) (29) see indic. refs.]

From other phenols or their relatives. [For formn. of C̄ from 2,4,6-trichloro-3-hydroxybenzaldehyde (6) by elimination of the aldehyde group with 50% aq. KOH at 60–70° for 4 hrs. (89.9% yield) see (6); from 2,4,6-trichloro-3-bromophenol (see below) or from 2,4,6-trichloro-3,5-dibromophenol (see below) by replacement of Br by H through use of Zn + AcOH see (9); from 2,4,6-tribromophenol [Beil. VI-203, VI_1-(107)] by replacement of all bromine by chlorine using Cl_2 in AcOH see (30).]

[For formn of C̄ from phenol-*p*-sulfonic acid [Beil. XI-241, XI_1-(55)] (10) or its alkali salts (31) (32) *in aq. soln with Cl_2 (100% yield (10)) see indic. refs.; from aq p-hydroxyazo*benzene [Beil. XVI-96, XVI_1-(233)] (75% yield (11)), from benzyl phenyl ether [Beil. VI-432, VI_1-(220)] (33), from *o*-hydroxybenzyl alcohol (saligenin) (1:1490) (34) with Cl_2 see indic. refs.; from dipotassium salt of salicylic acid (1:6780) with aq. KOCl (4 moles) see (8).]

From other miscellaneous sources. [For formn. of C̄ from aniline in HCl soln. with Cl_2 see (35); from 2,4,6-trichloroaniline via diazotization and subsequent hydrolysis as directed see (7); from indigo [Beil. XXIV-417, $XXIV_1$-(370)] in aq. suspension with Cl_2 see (36) (37); from benzene (1:7400) with Cl_2O see (38); from 2,4,6-trichlorophenyl hypochlorite (see below) by warming with acids or alkalies see (75).]

USES OF C̄ (OR ITS SALTS)

Although the topic cannot here be exhaustively pursued, the bactericidal, fungicidal, and general antiseptic action of C̄ or its salts has attracted much attention [for examples of useful articles in this general connection, see (39) (40) (41) (42) (43) (44) (45) (46); for patents on use of C̄ or its salts in the indicated fields see the following: for use of C̄ (with triaryl phosphates) as wood preservative (47), as preservative for glue (48), as insecticide and fungicide for board-like compns. from vegetable fibers (49), as bactericide (50) (51), as NaĀ for anti-mildew treatment of textiles (52), as textile asst. in mercerization (53); for various complexes contg. C̄ and intended for use as insecticides, etc., see (54) (55) (56)].

CHEMICAL BEHAVIOR OF C̄

Reduction of C̄. [The catalytic hydrogenation of C̄ apparently has not been extensively studied, but it is said (57) to be more stable toward H_2 + $PdCl_2$ than the corresponding 2,4,6-tribromophenol.]

Oxidation of C̄. C̄ on oxidn. gives various products according to circumstances [e.g., C̄ in 2 *N* H_2SO_4 on electrolytic oxidn. gives (58) 2,6-dichlorohydroquinone (3:4600); C̄ on oxidn. with CrO_3/AcOH (59) (60) (61) (62) (63), with cold fumg. HNO_3 (12) (63), with HNO_3/H_2SO_4 (64), with NO + NO_2 in alc. (65) (66) or AcOH (61), or with PbO_2 in AcOH or C_6H_6 (61) gives (*yields: 69% (59), 45% (60), 27% (61)*) 2,6-dichlorobenzoquinone-1,4 (3:3750) (note that this product may be accompanied (61) by more or less 2-chloro-6-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 134–135°, and 2,6-*bis*-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245°, which resemble the main prod. in appearance, composition, and behavior (61))].

[$\bar{C}$ on oxidn. with boilg. mixt. of conc. $HNO_3 + HCl$ gives (16) 2,3,5-trichlorobenzoquinone-1,4 (3:4672).]

[$\bar{C}$ on oxidn. with $ClSO_3H$ (67), with Cl_2 + fumg. H_2SO_4 followed by $ClSO_3H$ (68), with aqua regia (69) (70) (72), with $HCl + KClO_3$ (28) (16), with $CrO_3/AcOH$ (71) or $K_2Cr_2O_7/H_2SO_4$ (71) gives (90% yield (68)) 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[For study of oxidn. potential of $\bar{C}$ see (73).]

Nuclear substitution of $\bar{C}$. *Chlorination.* [$\bar{C}$ in HCl suspension with Cl_2 (74) or in AcOH soln. with $Ca(OCl)_2$ (75) gives 2,4,6-trichlorophenyl hypochlorite (2,4,4,6-tetrachlorocyclohexadien-2,5-one-1) [Beil. VII-147, VII_1-(96)], scales from ether/pet. ether, m.p. 122° (75) (10), 121–122° (76), 119° (74).]

[$\bar{C}$ with $Cl_2 + SbCl_5$ at not above 130° gives (77) 2,3,4,4,5,6-hexachlorocyclohexadien-2,5-one-1 ("hexachlorophenol") (3:3180), m.p. 107°.]

[$\bar{C}$ with Cl_2 (3) in pres. of I_2 at 40° (78), or $\bar{C}$ with Cl_2 in CCl_4 in pres. of $FeCl_3$ (79), or $\bar{C}$ with Cl_2 in pres. of $SbCl_3$, I_2, or $FeCl_3$ at 70–75° (80), gives 2,3,4,6-tetrachlorophenol (3:1687), m.p. 69°.]

[$\bar{C}$ with Cl_2 in pres. of $SbCl_3$, I_2, or $FeCl_3$ at 135–140° gives (81) pentachlorophenol (3:4850), m.p. 190°.]

[$\bar{C}$ with $FeCl_3$ (no details) yields (14) 1,2,3,5-tetrachlorobenzene (3:0915), m.p. 51°.]

Bromination. [$\bar{C}$ with Br_2/aq. KBr soln. as directed (82) (83) gives a monobromo derivative of $\bar{C}$ frequently designated as "trichlorophenol bromide"; which of the three structures 4-bromo-2,4,6-trichlorocyclohexadien-2,5-one-1, 2-bromo-2,4,6-trichlorocyclohexadien-2,5-one-1, or 2,4,6-trichlorophenyl hypobromite should be assigned to this prod. has never been decisively settled (83); however, on oxidn. with fumg. HNO_3 it gives (82) 2,6-dichlorobenzoquinone-1,4 (3:3750) and with conc. H_2SO_4 at 100° isomerizes (82) to 3-bromo-2,4,6-trichlorophenol, m.p. 73° (9) (corresp. benzoate, m.p. 117° (82)).]

[$\bar{C}$ with Br_2 (large excess) + Fe powder at room temp. for 24 hrs. gives (100% yield (84)) cf. (85) 3,5-dibromo-2,4,6-trichlorophenol, cryst. from AcOH, m.p. 204° cor. (corresp. methyl ether, m.p. 127°; corresp. benzoate, m.p. 196° (84)).]

Nitration. [The direct nitration of $\bar{C}$ has not been reported, presumably because nitration reagents readily oxidize free $\bar{C}$ to 2,6-dichlorobenzoquinone-1,4 (3:3750) (see above under oxidn. of $\bar{C}$). — However, both possible nitration products have been obtained by indirect means: for 3-nitro-2,4,6-trichlorophenol, m.p. 71–72°, see (86); for 3,5-dinitro-2,4,6-trichlorophenol, m.p. 165–167°, see (87).]

Sulfonation. [$\bar{C}$ with fumg. H_2SO_4 (65% SO_3) at 50° gives (93% yield (88) 2,4,6-trichlorophenolsulfonic acid-3.]

Miscellaneous. [$\bar{C}$ with $SCl_2 + AlCl_3$ in CS_2 or CCl_4 gives (89) a product, m.p. 285°, which may be 3,3'-dihydroxy-2,4,6,2',4',6'-hexachlorodiphenyl sulfide.]

Reactions of the phenolic group of $\bar{C}$. (See also under Ⓓ's below.)

Acidic character of $\bar{C}$. $\bar{C}$ in aq. behaves as an acid and can be titrated with $N/10$ aq. NaOH (3); Neut. Eq. = 197.5. — [Data on dissoc. const. of $\bar{C}$ include the following: in aq. at 25° 1.0×10^{-7} (90), 3.9×10^{-7} (2) cf. (91) (92). — For study of acid strength of $\bar{C}$ in formamide see (93). — For study of exchange reaction of $\bar{C}$ with heavy water see (94).]

Salts of $\bar{C}$. [$NH_4\bar{A}$: spar. sol. cold aq., eas. sol. hot aq. (22), somewhat spar. sol. alc. (24); loses NH_3 in air (12). — $K\bar{A}$, $\frac{1}{2}H_2O$: (24) (12). — $Na\bar{A}$: prepn. (95), behavior with I_2 in various solvents (95) (96), behavior with chloroacetone (3:5425) giving acetonyl 2,4,6-trichlorophenyl ether, m.p. 75° (96).]

$Mg\bar{A}.2H_2O$: eas. sol. aq. (12). — $Ba\bar{A}_2.4H_2O$: spar. sol. aq. (12). — $Pb\bar{A}_2$ (12).

$Ag\bar{A}.H_2O$: yellow (97) [study of decompositions (98) (96) (99)].

Etherification of $\bar{C}$. (See also below under Ⓓ's.)

[C̄ with 1,2-dibromoethane (ethylene dibromide) in alk. soln. gives (100) β-bromoethyl 2,4,6-trichlorophenyl ether, m p. 47–48°. — C̄ with ethylene oxide (1:6105) in alc. NaOEt gives (101) β-hydroxyethyl 2,4,6-trichlorophenyl ether, m.p. 77° (101) (for study of rate of this reaction see (102)) — C̄ (as NaĀ) with benz-o-chlorophenylimino-chloride gives (103) N-(o-chlorophenyl)benzimino 2,4,6-trichlorophenyl ether, m.p. 99–100°, which at 250–270° for 2 hrs rearr. (103) to the N-benzoyl derivative (m.p. 131–132°) of 2,4,6,2'-tetrachloro-diphenylamine. — C̄ with 2,4,6-trichlorobenzyl chloride + NaOH gives (104) 2,4,6-trichlorobenzyl 2,4,6-trichlorophenyl ether, m.p. 101–103°]

Esterification of C̄. (See also below under Ⓓ's.)

[C̄ with $SOCl_2$ in pyridine + C_6H_6 gives (4) *bis*-(2,4,6-trichlorophenyl) sulfite, cryst. from C_6H_6, m p 87–88°; note, however, that this prod is unstable and even within a few hours reverts to C̄.]

[C̄ with PCl_5 in C_6H_6 gives (105) *bis*-(2,4,6-trichloropnenoxy)phosphoryl chloride, $(C_6H_2OCl_3)P(O)Cl$, cryst. from C_6H_6, m.p. 126–129° (105). (Note that C̄ with PCl_5 in s.t. at 200–300° gives also (106) some 1,2,3,5-tetrachlorobenzene (3:0915).) — C̄ (3 moles) with $POCl_3$ (1 mole) refluxed several days gives (107) *tris*-(2,4,6-trichlorophenyl) phosphate, m.p. 201° (107).]

[C̄ (2 moles) with $COCl_2$ (3:5000) in aq. alk. gives (108) *bis*-(2,4,6-trichlorophenyl) carbonate, m.p. 153–154° (109).]

Ⓓ **2,4,6-Trichlorophenyl methyl ether** (2,4,6-trichloroanisole) [Beil. VI-192]: cryst. from alc., m.p. 61–62° (9), 60° (110) (111), 59.5° (112); b p. 240° cor. at 738 mm. (110) cf. (87). [From C̄ with Me_2SO_4 + 15% KOH (87); for crystallographic data see (82); for attempted cleavage with pyridine or piperidine see (113); for nitration see (87)]

Ⓓ **2,4,6-Trichlorophenyl ethyl ether** (2,4,6-trichlorophenetole) [Beil VI-192, VI₁-(104)]: m.p. 43–44° (12), b.p. 246° (12). [From KĀ + EtI (12) or from AgĀ + EtI (98).]

—— **2,4,6-Trichlorophenyl acetate:** oil, b.p. 261–262° (114). [From C̄ with AcCl (114).]

Ⓓ **2,4,6-Trichlorophenyl benzoate** [Beil. IX-117]. m.p. 75.5° (9), 74° (115), 73–74° (6), 70° (14). [From C̄ with benzoyl chloride (3:6240) in pres of aq. NaOH (115) (9); for study of rate of benzoylation of C̄ at 25° and 85° see (116).]

—— **2,4,6-Trichlorophenyl o-nitrobenzoate:** unreported.

—— **2,4,6-Trichlorophenyl m-nitrobenzoate:** unreported.

Ⓓ **2,4,6-Trichlorophenyl p-nitrobenzoate:** m p. 106° (115).

—— **2,4,6-Trichlorophenyl 3,5-dinitrobenzoate:** unreported.

Ⓓ **2,4,6-Trichlorophenyl benzenesulfonate:** m p. 66° (117). [From C̄ with benzenesulfonyl chloride in aq. alk. (117)]

Ⓓ **2,4,6-Trichlorophenyl o-nitrobenzenesulfonate:** m.p. 142° (118). [From C̄ with o-nitrobenzenesulfonyl chloride + K_2CO_3 in acetone (118)]

—— **2,4,6-Trichlorophenyl p-toluenesulfonate:** unreported.

—— **2,4,6-Trichlorophenyl phenyl ether:** unreported.

Ⓓ **2,4,6-Trichlorophenyl 2,4-dinitrophenyl ether:** m.p. 136° (119). [From C̄ with 2,4-dinitrochlorobenzene in alc. alk. (119)]

—— **2,4,6-Trichlorophenyl benzyl ether:** unreported.

—— **2,4,6-Trichlorophenyl p-nitrobenzyl ether:** unreported.

Ⓓ **2,4,6-Trichlorophenoxyacetic acid:** m p 177° (120).

—— **2,4,6-Trichlorophenyl N-phenylcarbamate:** unreported.

Ⓓ **2,4,6-Trichlorophenyl N-(p-bromophenyl)carbamate:** pl. from C_6H_6 + EtOAc, m p. 162–164° cor. (121). [From C̄ with p-bromobenzazide (121) in lgr. (121).]

Ⓓ **2,4,6-Trichlorophenyl N-(p-iodophenyl)carbamate:** m p. 172–173° (122). [From C̄ with p-iodobenzazide (122) in lgr. (122).]

Ⓓ 2,4,6-Trichlorophenyl *N*-(*m*-nitrophenyl)carbamate: white rods from lgr., m.p. 165–167° u.c.; 169–170° cor. (123). [From C̄ with *m*-nitrobenzazide (123) in lgr. (123).]

Ⓓ 2,4,6-Trichlorophenyl *N*-(*p*-nitrophenyl)carbamate: pale yel. rods from lgr., m.p. 166° cor. (124). [From C̄ with *p*-nitrobenzazide (124) in lgr. (124).]

—— 2,4,6-Trichlorophenyl *N*-(3,5-dinitrophenyl)carbamate: unreported.

Ⓓ 2,4,6-Trichlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: yel. pr. from lgr. or EtOAc, m.p. 195–196° u.c., 201–202° cor. (125). [From C̄ with 3,5-dinitro-4-methylbenzazide (125) in lgr. (125).]

—— 2,4,6-Trichlorophenyl *N*-(α-naphthyl)carbamate: unreported.

Ⓓ 2,4,6-Trichlorophenyl *N*-(β-naphthyl)carbamate: pr. from lgr., m.p. 157–158° u.c., 161–162° cor. (126). [From C̄ with β-naphthyl isocyanate (126) or β-naphthazide (126) in lgr. (126).]

Ⓓ 2,4,6-Trichlorophenyl *N,N*-diphenylcarbamate: m.p. 143° (127). [From C̄ with *N,N*-diphenylcarbamyl chloride (127).]

3:1673 (1) Jaeger, *Z. anorg. allgem. Chem.* **101**, 129 (1917). (2) Tiessens, *Rec. trav. chim.* **48**, 1068 (1929). (3) Tiessens, *Rec. trav. chim.* **50**, 115–116 (1931). (4) Richter, *Ber.* **49**, 2344 (1916). (5) Hassel, Naeshagen, *Z. physik. Chem.* **B-12**, 86 (1931). (6) Lock, *Monatsh.* **55**, 312 (1930). (7) Cain, Norman, *J. Chem. Soc.* **89**, 23–24 (1906). (8) Lassar-Cohn, Schultze, *Ber.* **38**, 3301 (1905). (9) Kohn, Fink, *Monatsh.* **58**, 76, 87–89 (1931). (10) Datta, Mitter, *J. Am. Chem. Soc.* **41**, 2032 (1919).

(11) Schmidt, *J. prakt. Chem.* (2) **85**, 237–238 (1912). (12) Faust, *Ann.* **149**, 149–155 (1869). (13) Hrynakowski, Szmyt, *Z. physik. Chem.* **A-182**, 111, 114–115 (1938). (14) Daccomo, *Ber.* **18**, 1163–1164 (1885). (15) Bennett, Wain, *J. Chem. Soc.* **1936**, 1118. (16) Leger, *Compt. rend.* **146**, 696 (1908); *Bull. soc. chim.* (4) **3**, 578–582 (1908). (17) van Erp, *Rec. trav. chim.* **30**, 281 Note (1911). (18) Takagi, Ishimasa, *J. Pharm. Soc. Japan* **1925**, No. 517, 17–18; *Cent.* **1926**, I 182; *C.A.* **20**, 2669 (1926). (19) Giua, Cherchi, *Gazz. chim. ital.* **49**, II 269, 282 (1919). (20) Küster, Würfel, *Z. physik. Chem.* **50**, 74–80 (1904).

(21) Efremov, *Ann. inst. anal. phys.-chim.* (*U.S.S.R.*) **5**, 75–141 (1931); *Cent.* **1934**, I 3734; *C.A.* **27**, 277 (1933). (22) Laurent, *Ann. chim.* (2) **63**, 27–33 (1836); (3) **3**, 206–211 (1841); *Ann.* **23**, 60–71 (1837); **43**, 209–212 (1842). (23) Chulkov, Parini, Staroselets, *Org. Chem. Ind.* (*U.S.S.R.*) **3**, 97–101 (1937); *Cent.* **1938**, I 1419; *C.A.* **31**, 4967 (1937). (24) Chandelon, *Bull. soc. chim.* (2) **38**, 116–124 (1882). (25) Chabrier de la Saulniere, *Ann. chim.* (11) **17**, 353–370 (1942); *C.A.* **38**, 3256 (1944); *Compt. rend.* **213**, 400–402 (1941); *C.A.* **37**, 2010 (1943). (26) Likhosherstov, *J. Russ. Phys.-Chem. Soc.* **61**, 1019–1023, 1025–1028 (1929); *Cent.* **1930**, I 1924; *C.A.* **24**, 836 (1930). (27) Marsh, *J. Chem. Soc.* **1927**, 3164. (28) Hofmann, *Ann.* **52**, 57, 62 (1844). (29) Graebe, *Ann.* **146**, 8, 12 (1868). (30) Benedikt, Schmidt, *Monatsh.* **4**, 604 (1883).

(31) Tanaka, Kutani, *J. Pharm. Soc. Japan* No. **541**, 196–199 (1927); *Cent.* **1927**, *II 51*; *C.A.* [illegible] 449–450 (1865). (33) Sintenis, *Ann.* **161**, [illegible]

[illegible] 7, 29–31 (1941); *C.A.* **35**, 7719 (1941). [illegible] rig. **145**, 425–438 (1940); *C.A.* **35**, 8008 [illegible] 28, 38 (1940); *C.A.* **34**, 4605 (1940).

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[illegible] 52) British Dye- [illegible] 7; *C.A.* **21**, 3433

(1927). (53) Brodersen, Waldmüller, Ger. 576,384, May 10, 1933; *Cent.* **1933**, II 473; *C.A.* **27**, 3833 (1933). (54) Urbschat, Heckmanns (to I.G.), Ger. 552,150, June 11, 1932; *Cent.* **1932**, II 1500; *C.A.* **26**, 4427 (1932). (55) Heckmanns, Urbschat (to I G), Ger. 545,612, March 4, 1932; *Cent.* **1932**, II 759, *C A.* **26**, 3610 (1932). (56) Brodersen, Ext (to I.G), Ger. 412,432, March 28, 1927; *Cent* **1927**, II 487; not in *C.A.* ... *Yougoslav.* **4**, 187–195 (1933); *Cent* **1934**, II 2354; [C. ... Stocker, *Ber.* **47**, 2016 (1914) (59) Conant, Fieser, *J. Am* ... **45** ... Hunter, Morse, *J. Am. Chem Soc.* **55**, 3701, 3704 (1933).

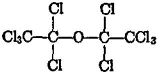
(61) Hunter, Morse, *J. Am. Chem. Soc* **48**, 1615–1624 (1926). (62) Kehrmann, Tiessler, *J. prakt. Chem.* (2) **40**, 481 (1889) (63) Ling, *J. Chem Soc.* **61**, 559 (1892). (64) Guareschi, Daccomo, *Ber* **18**, 1170 (1885) (65) Weselsky, *Ber.* **3**, 646 (1870). (66) Lampert, *J. prakt. Chem* (2) **33**, 381 (1886) (67) Schuloff, Pollak, *C*...
1510; [*C.A.* **26**, 5086 (1932)]. (68) Heimberg, Ge...
C.A. **25**, 1266 (1931)...
Ger. 256,034, Feb ...
(71) Levy, Schul...
(1916). (73) Fiese...
(1883). (75) Zinck...
103, 226 (1913).
Monatsh. **48**, 233–244 (1927). (79) Michael, Buschmann, Ger. 527,393, June 19, 1931, *Cent.* **1931**, II 2785; [*C.A.* **25**, 4556 (1931)]. (80) Barral, Grosfillex, *Bull. soc. chim.* (3) **27**, 1175–1176 (1902).

(81) Barral, Jambon, *Bull. soc. chim.* (3) **23**, 822–825 (1900). (82) Kohn, Rabinowitsch, *Monatsh.* **48**, 347–356 (1927). (83) Lauer, *J. Am. Chem. Soc* **48**, 442–451 (1926). (84) Kohn, Dömötör, *Monatsh.* **47**, 212–214 (1926). (85) Korczynski, Reinholz, Schmidt, *Roczniki Chem.* **9**, 731–740 (1929); *Cent.* **1930**, I 2076, [*C A* **24**, 1858 (1930)] (86) Fox, Turner, *J. Chem. Soc.* **1930**, 1860. (87) Kohn, Heller, *Monatsh* **46**, 95 (1925). (88) Weiler, Better (to I.G.), Ger. 557,450, Aug. 24, 1931; *Cent.* **1932**, II 2370–2371; *C A.* **27**, 735 (1933) (89) Muth (to I G.), Ger. 583,055, Aug 28, 1933, *Cent.* **1933**, II 3883, *C.A* **28**, 179 (1934). (90) Hantzsch, *Ber.* **32**, 3070 (1899).

... ay, Gordon, *J. Am Chem. Soc.* **57**, 110–111 ... (1936). (94) Small, Wolfenden, *J. Chem.* ... *m. Soc.* **43**, 154–159 (1921). (96) Hunter, ... (97) Hantzsch, Scholtze, *Ber.* **40**, 4879 (1907). (98) Hunter, Olson, Daniels, *J Am Chem. Soc.* **38**, 1761–1771 (1916). (99) Hunter, Rathmann, *J. Gen. Chem.* **7**, 2230–2231 (1937), *Cent.* **1938**, I 3331; *C A* **32**, 518 (1938). (100) ... (1915). ... (1914). (102) Boyd, Thomas, *J. Chem. Soc.* **115**, ... **1929**, 570. (104) Holt (to du Pont Co.), U.S. ... *C A.* **31**, 3065 (1937). (105) Anschütz, Boedeker, ... *Cent* **1896**, I 100 (107) Breusch, Keskin, *Rev. faculté sci. univ. Istanbul* **7-A**, 182–189 (1942), *C.A.* **38**, 1483 (1944). (108) Barral, Morel, *Bull. soc. chim.* (3) **21**, 724–726 (1899). (109) Barral, *Compt. rend.* **138**, 911 (1904). (110) Hugounenq, *Ann. chim* (6) **20**, 521–524 (1890).

(111) Durrans, *J. Chem. Soc.* **123**, 1426 (1923). (112) Lock, *Monatsh.* **62**, 185 (1933). (113) Cahn, *J. Chem. Soc.* **1931**, 1122. (114) Fischer, *Ann. Suppl.* **7**, 184–185 (1870). (115) Raiford, Taft, Lankelma, *J. Am. Chem. Soc.* **46**, 2056 (1924). (116) Bernoulli, St. Goar, *Helv. Chim. Acta* **9**, 756–757 (1926) (117) Minovici, *Bul soc. sci. Bucuresci* **2**, 131 (1893). (118) Tozer, Smiles, *J. Chem. Soc.* **1938**, 2056. (119) Bost, Nicholson, *J. Am Chem. Soc.* **57**, 2368–2369 (1935). (120) Bischoff, *Ber.* **33**, 1605 (1900)

(121) Sah, Cheng, *Rec. trav. chim.* **58**, 592–593 (1939). (122) Sah, Young, *Rec. trav. chim.* **59**, 357–363 (1940), *C.A.* **35**, 4363 (1941). (123) Sah, Woo, *Rec. trav. chim.* **58**, 1013–1015 (1939). (124) Sah, Cheng, *Rec. trav. chim.* **58**, 595–597 (1939). (125) Sah, *Rec. trav. chim.* **58**, 587, 589 (1939). (126) Sah, *Rec. trav. chim.* **58**, 454–458 (1939). (127) Korczynski, *Gazz. chim. ital.* **53**, 96–97 (1923).

3:1676 DECACHLORODIETHYL ETHER (*bis*-(Pentachloroethyl) ether; "Perchloroether")  C_4OCl_{10} Beil. II - 210 II_1— II_2—

M.P. 69° (1) $D_{-}^{14.5} = 1.900$ (2)

[For crystallog. data see (3).]

[For prepn. of C̄ from abs. diethyl ether (1:6110) with excess dry Cl_2 in direct sunlight see (1).]

C̄ on boilg. decomposes (2) into trichloroacetyl chloride (3:5420) and hexachloroethane (3:4835).

C̄ with conc. H_2SO_4 at 240° is slowly attacked yielding (2) trichloroacetyl chloride (3:5420).

C̄ with alc. K_2S loses 2 atoms of chlorine yielding (2) di-(trichlorovinyl) ether (3:6373).

C̄ with metallic potassium on htg. detonates; in this behavior C̄ behaves toward alkali metals like many other highly halogenated compounds.

Note that all these data on C̄ are very old; no later studies of C̄ are reported in the literature.

3:1676 (1) Regnault, *Ann.* **34**, 27–29 (1840). (2) Malaguti, *Ann. chim.* (3) **16**, 13–28 (1846). (3) Nickles, *Ann. chim.* (3) **22**, 29 (1848).

3:1685 CHLOROPROPIOLIC ACID Cl.C≡C.COOH C_3HO_2Cl Beil. II - 478 II_1— II_2-(451)

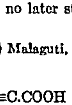
M.P. 69–70° (1)

Colorless cryst. from pet. eth.; eas. sol. ether; eas. vol. (even in desiccator). Very irritating and poisonous; salts extremely toxic (1). — Stable in dry state at room temperature.

[For prepn. from propiolic ac. [Beil. II-477] by actn. of KOH/KOCl soln. at 0° see (1) (2).]

C̄ on htg. with $Ba(OH)_2$ soln. yields chloroacetylene (3:7000) + $BaCO_3$ while acidification and ether extraction of the aq. layer yields malonic ac. (1:0480), m.p. 133–134° (1). [An alk. soln. of C̄ on stdg. is also partly converted to malonic ac. (1).]

3:1685 (1) Straus, Kollek, Heyn, *Ber.* **63**, 1876–1877 (1930). (2) Brit. 333,946, Sept. 18, 1930; *Cent.* **1931**, I 523.

3:1687 2,3,4,6-TETRACHLOROPHENOL  $C_6H_2OCl_4$ Beil. VI - 193 VI_1— VI_2-(182)

M.P.	**70°**	(1) (2) (3)	**B.P.**	**164°**	at 23 mm. (4)
	69–70°	(4)		**160.5°**	at 21 mm. (4)
	68–69°	(5) (6)		**159°**	at 20 mm. (4)
	67.5–68°	(7)		**157°**	at 19 mm. (4)
	67–69°	(8)		**155°**	at 18 mm. (4)
	67–68°	(9)		**152.5°**	at 17 mm. (4)
	67°	(10) (11)		**150°**	at 16 mm. (4)
	65.5°	(12)			
	65–66°	(13)			

Ndls. from lgr., AcOH, or ether. — Almost insol. cold aq.; spar. sol. hot aq.; but volatile with steam. — Eas. sol. alc., C_6H_6, $CHCl_3$, CS_2, lgr.; fairly sol. hot pet. eth. — Odorless at ord. temp.

PREPARATION OF $\bar{C}$

[For prepn. of $\bar{C}$ from phenol (1:1420) with Cl_2 at 80° for 14 days (7) or with Cl_2 in pres. of 2–3% I_2 or 4–5% $SbCl_3$ or 5–6% $FeCl_3$ for shorter periods (7), from sodium phenolate with SO_2Cl_2 (13), or from 2,4,6-trichlorophenol (3:1673) with Cl_2 (1) in pres. of I_2 at 40° (8) or with Cl_2 in CCl_4 soln. in pres. of $FeCl_3$ (14), see indic. refs.]

[For formn. of $\bar{C}$ from 3,5,6-trichloro-2-hydroxybenzoic acid (3,5,6-trichlorosalicylic acid) (5) with Cl_2 in 30% AcOH see (5); from 2,4,5,6-tetrachloro-3-hydroxybenzoic acid [Beil. X-144] (11) by htg. with lime see (11); from 2,4,5,6-tetrachloro-3-hydroxybenzaldehyde (6) with 50% aq. KOH at 100° for 2 hrs. (the CO group being eliminated as K formate) see (6); from *o*-(2,4,5,6-tetrachloro-3-hydroxybenzoyl)benzoic acid (3) by cleavage with conc. H_2SO_4 see (3).]

[For formn. of $\bar{C}$ from 1,2,4,4,5,6,6-heptachlorocyclohexen-1-one-3 [Beil. VII-51] by reduction with $SnCl_2/HCl/AcOH$ (4) or with KI/AcOH or Na_2SO_3/AcOH see (12); from "6-hydroxyphenylene diazosulfide" with Cl_2 in AcOH followed by reduction with $SnCl_2$ see (10).]

USES OF $\bar{C}$ (OR ITS SALTS)

[For patents on use of $\bar{C}$ (or its salts) as bactericide (15) (16) in preservation of rubber latex (17), as insecticide (18), or in triphenyl phosphate as wood preservative (19) see indic. refs.]

[For general articles on $\bar{C}$ (or its salts) as bactericides (20), fungicides (21) (27) for paint (22) or leather (23) (24) (25) (26), or in preservation of brine samples for analysis (28) see indic. refs.]

PHYSIOLOGICAL EFFECTS OF $\bar{C}$ (OR ITS SALTS)

[For studies on dermatitis from $\bar{C}$ or its salts see (29) (30); for report on toxicity of $\bar{C}$ in leather see (31).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Action of chlorine. [$\bar{C}$ with Cl_2 in AcOH gives (4) (12) 1,2,4,4,5,6,6-heptachlorocyclohexen-1-one-3 [Beil. VII-51].]

Action of bromine. $\bar{C}$ with Br_2 (1 mole) in pres. of Fe powder gives (8) 5-bromo-2,3,4,6-tetrachlorophenol [Beil. VI_1-(106)], cryst. from AcOH, m.p. 197° (8) (32), 192° (33) (corresp. acetyl deriv., m.p. 144° (33); corresp. benzoyl deriv., m.p. 169° (33)).

Action of nitric acid. [$\bar{C}$ with fumg. HNO_3 (5 wt. parts) is oxidized (70% yield (4)) (12) to 2,3,5-trichlorobenzoquinone-1,4 (3:4672). — Note, however, that the mononitro deriv. of $\bar{C}$, viz., 5-nitro-2,3,4,6-tetrachlorophenol, ndls. from C_6H_6, m.p. 122°, has been obtd. (8) by HBr cleavage of the corresp. methyl ether (see below).]

Behavior of $\bar{C}$ as an acid. $\bar{C}$ in aq. behaves as an acid, K at 25° = 4.2×10^{-6} (2) cf. (34), and can be titrated with $N/10$ aq. NaOH (1); Neut. Eq = 232. — [For prepn. of alk. salts of $\bar{C}$ by neutralization in mixtures of org. solvents see (35); for uses of salts of $\bar{C}$ see above.]

Miscellaneous reactions of $\bar{C}$. [$\bar{C}$ (as $K\bar{A}$) in conc. aq. soln. with $COCl_2$ (3:5000) in toluene gives (36) *bis*-(2,3,4,6-tetrachlorophenyl) carbonate, m.p. 155–156° (36).]

Ⓓ **2,3,4,6-Tetrachlorophenyl methyl ether** (2,3,4,6-tetrachloroanisole): ndls. from MeOH, m.p. 64–65° (4), 60° (8), b.p. 266–270° u.c. at 244 mm. (8). [From C̄ with MeI in MeOH/NaOMe soln. (4) cf. (8). — Note that this prod. on nitration with 7–8 wt. pts. fumg. HNO_3 gives 5-nitro-2,3,4,6-tetrachloroanisole, m.p. 58° (8).]

Ⓓ **2,3,4,6-Tetrachlorophenyl ethyl ether** (2,3,4,6-tetrachlorophenetole): ndls. from alc., m.p. 59–60° (4), 55° (6). [From C̄ with EtI in EtOH/NaOEt soln. (4); also indirectly (6).]

Ⓓ **2,3,4,6-Tetrachlorophenyl acetate**: cryst. from alc., m.p. 66° (5), 65–66° (4), 59° (12). [From C̄ with Ac_2O (4) or with AcCl (12).]

Ⓓ **2,3,4,6-Tetrachlorophenyl benzoate**: cryst. from alc., m.p. 116° (10) (13) (3), 115° (4), 114.5° (12), 113–115° (11). [From C̄ as NaĀ with BzCl (4). — Note that this prod. depresses m.p. (110°) of the corresp. benzoate from 2,3,4,5-tetrachlorophenol (3:3523) (9).]

Ⓓ **2,3,4,6-Tetrachlorophenyl *N*-phenylcarbamate**: ndls. from alc., m.p. 141–142° (4). [From C̄ with phenyl isocyanate in C_6H_6 24 hrs. at room temp. (4).]

3:1687 (1) Tiessens, *Rec. trav. chim.* **50**, 116, 119 (1931). (2) Tiessens, *Rec. trav. chim.* **48**, 1068 (1929). (3) Fries, Auffenberg, *Ber.* **53**, 24, 28 (1920). (4) Biltz, Giese, *Ber.* **37**, 4013–4017 (1904). (5) Farinholt, Stuart, Twiss, *J. Am. Chem. Soc.* **62**, 1239, 1241 (1940). (6) Lock, Nottes, *Monatsh.* **67**, 323 (1936). (7) Barral, Grosfillex, *Bull. soc. chim.* (3) **27**, 1174–1178 (1902). (8) Kohn, Pfeifer, *Monatsh.* **48**, 233–236 (1927). (9) Holleman, *Rec. trav. chim.* **40**, 318–319 (1921). (10) Fries, Vorbrodt, Siebert, *Ann.* **454**, 190 (1927).

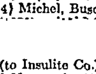
(11) Zincke, Walbaum, *Ann.* **261**, 239–246 (1891). (12) Zincke, Schaum, *Ber.* **27**, 549 (1894). (13) Durrans, *J. Chem. Soc.* **121**, 47 (1922). (14) Michel, Buschmann (to I.G.), Ger. 527,393, [illegible]

[illegible] 1942, I 2831; *C.A.* **36**, 1207 (1942). (18) Ellis (to Insulite Co.), U.S. 2,161,654, June 6, 1939; *Cent.* **1939**, II 4620; *C.A.* **33**, 7568 (1939). (19) Norton (to Dow Chem. Co.) U.S. 2,304,013, Dec. 1, 1942; *C.A.* **37**, 2908 (1943). (20) Melnikor, Aretesyan, Rokitskaya, *Compt. rend. acad. sci. U.R.S.S.* **31**, 123–124 (1941); *Cent.* **1942**, II 2055; *C.A.* **37**, 950–951 (1943).

(21) Mallman, Michael, *Mich. State Coll. Agr. Expt. Sta., Tech. Bull.* **174** (1940); *C.A.* **35**, [illegible] (1940); *C.A.* **36**, 847 (1942).

(31) Lollar, *J. Am. Leather Chem. Assoc.* **39**, 203–209 (1944); *C.A.* **38**, 6594 (1944). (32) Kohn, Zandmann, *Monatsh.* **47**, 372–373 (1926). (33) McCombie, Ward, *J. Chem. Soc.* **103**, 2005 (1913). (34) Murray, Gordon, *J. Am. Chem. Soc.* **57**, 110–111 (1935). (35) Mills (to Dow Chem. Co.), U.S. 1,955,080, April 17, 1934, *Cent.* **1934**, II 1991; *C.A.* **28**, 3743 (1934). (36) Barral, *Compt. rend.* **138**, 981 (1904).

3:1690 2,6-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII - 237 VII_1-(134)



M.P. 71° (1)
70–71° (2)
70° (3)
69–70° (4) (5)

Colorless cryst. from pet. ether (b.p. 40–60°) or lgr.

[For prepn. of C̄ from 2,6-dichlorotoluene (3:6270) by oxidn. with $MnO_2 + H_2SO_4$ see (2); for prepn. of C̄ from 2,6-dichlorobenzaldehyde diethylacetal (see below) by hydrolysis on shaking with dil. HCl see (6).]

[C̄ on reduction would presumably yield 2,6-dichlorobenzyl alc., but this prod. is unreported in the literature.]

C̄ in alk. suspension on oxidn. with air gives (7) 2,6-dichlorobenzoic acid (3:4200), m.p. 144°.

[C̄ (fused) with Cl_2 in brilliant artificial light gives (58% yield (8)) 2,6-dichlorobenzoyl chloride, b.p. 126–128° at 18 mm. — C̄ with PCl_5 at 160° gives (90% yield (9)) (4) (5) 2,6-dichlorobenzal (di)chloride (3:9398) oil, b.p. 124–126° at 16 mm. (9), accompanied in some preparations (4) (5) by some *bis*-(α,2,6-trichlorobenzyl) ether, m.p. 180–185° (4) (5).]

[C̄ with alkali sulfite (1 mole) under press. reacts at one of the two halogen atoms giving (2) 6-chlorobenzaldehydesulfonic acid-2 [Beil. XI-324] — C̄ with alkali sulfite (2 moles) under press. gives (2) benzaldehyde disulfonic acid-2,6 [Beil. XI-326].]

C̄ disslvd. in 7–8 wt. pts. conc. H_2SO_4, and at 10–15° mononitrated with a mixt. of fumg. HNO_3 + conc. H_2SO_4, poured into aq. gives (yield not stated (10)) (2) 2,6-dichloro-3-nitrobenzaldehyde [Beil. VII-263], pl. from CS_2 (10) or lfts. from C_6H_6 (2), m.p. 76° (10), 76–77° (2) (corresp. α-oxime, m.p. 156–157° (10), β-oxime, m.p. 154–155° (10); note that a mixt. of the two oximes melts 128–130° (10)) — [Note that no dinitro-2,6-dichlorobenzaldehyde has been reported; also that the m.p.'s of certain of the isomeric mononitrodichlorobenzaldehydes are very close to the above mononitration prod.: e.g., 2,4-dichloro-6-nitrobenzaldehyde (from 2,4-dichlorobenzaldehyde 3:1800) has m.p. 74–75°; 2,5-dichloro-3-nitrobenzaldehyde (from 2,5-dichlorobenzaldehyde 3:1145) has m.p. 66.5–67°; 3,4-dichloro-6-nitrobenzaldehyde (from 3,4-dichlorobenzaldehyde 3:0550) has m.p. 73°.]

[C̄ on sulfonation gives (2) 2,6-dichlorobenzaldehydesulfonic acid-3 [Beil. XI-325].]

[C̄ with 50% KOH at 100° for 5 hrs. under N_2 undergoes cleavage of the aldehyde group giving (84% yield (11)) *m*-dichlorobenzene (3:5960) q.v. and the corresp. K formate.]

[C̄ with aq. alc. hydrazine sulfate gives (86% yield (18)) 2,6-dichlorobenzaldazine, m.p. 153° cor.; but this prod. or C̄ with hydrazine hydrate refluxed 5 hrs. gives 2,6-dichlorobenzaldehyde hydrazone, m.p. 134°, which by Wolff-Kishner reduction gives (80% yield (18)) 2,6-dichlorotoluene (3:6270).]

[C̄ with EtOH contg. 1½ wt. % dry HCl refluxed 24 hrs. gives (13.6% yield (6)) 2,6-dichlorobenzaldehyde diethylacetal, oil, b.p. 142–144° at 10 mm., m.p. −1° (6); this prod. with dil. HCl readily hydrolyzes back to C̄ + EtOH.]

[C̄ with β-naphthol (2 moles) in AcOH with 30% HBr in AcOH at 100° for 2 hrs. or at room temp. for 24 hrs. condenses and ring-closes giving (88% yield (8)) 9-(2,6-dichlorophenyl)-1,2,7,8-dibenzoxanthane ($C_{27}H_{16}OCl_2$), cryst. from lgr., m.p. 264–265° (8). — Note that C̄ with β-thionaphthol (2 moles) under similar conditions yields a prod. $C_{27}H_{18}S_2Cl_2$, of unknown structure.]

C̄ with anhydrous NaOAc + Ac_2O in Perkin synthesis (12) (13) (1), or C̄ with malonic acid in AcOH (13) gives (yields: 81–83% (12), 80% (1), 18% (13)) 2,6-dichlorocinnamic acid [Beil. IX$_1$-(239)], cryst. from AcOH, m.p. 196° (12), 193° (13), 183° (1); note that in this reaction some 2,6-dichlorobenzal diacetate [Beil. VII$_1$-(134)], ndls. from lgr., m.p. 85° (1), is sometimes formed.

C̄ appears to behave normally with RMgX reactants [e.g., C̄ with MeMgI in dry ether followed by usual hydrolysis gives (68.6% yield (14)) 2,6-dichlorophenyl-methyl-carbinol,

m.p. 34–35°, b.p. 137–138° at 17 mm., 134–136° at 13 mm. (corresp. benzoate, m.p. 77°); C̄ with C_6H_5MgBr similarly gives in good yield (1) 2,6-dichlorophenyl-phenyl-carbinol, m.p. 57° (corresp. acetate, m.p. 105°)]. [For conversion of C̄ to 2,6-dichlorostyrene (16) (17) via formn. of 2,6-dichlorophenyl-methyl-carbinol (above) and dehydration of latter with $KHSO_4$ (31.5% yield (16)) see indic. refs.]

C̄ with aniline readily condenses yielding (1) 2,6-dichlorobenzaldehyde anil, m.p. 64–65°.

Ⓓ **2,6-Dichlorobenzaldoxime:** colorless ndls. from C_6H_6 (10) or lgr. (1), m.p. 149–150° (10), 146–147° (1). [From C̄ with $NH_2OH.HCl$ + Na_2CO_3 in dil. alc. at 100° for 5 hrs. (10) cf. (1); with cold Ac_2O this prod. gives an acetyl deriv., m.p. 51° (10); with boilg. Ac_2O for 5 min. the oxime loses H_2O giving (1) 2,6-dichlorobenzonitrile [Beil. IX-343, IX_1-(141)], ndls. from lgr. or by sublimation, m.p. 143° (1), 144.5–146.5° (15).]

—— **2,6-Dichlorobenzaldehyde phenylhydrazone:** unreported.

—— **2,6-Dichlorobenzaldehyde *o*-nitrophenylhydrazone:** m.p. 154° (1).

—— **2,6-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.

—— **2,6-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unreported.

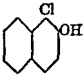
—— **2,6-Dichlorobenzaldehyde *p*-bromophenylhydrazone:** m.p. 142° (1).

—— **2,6-Dichlorobenzaldehyde semicarbazone:** unreported.

3:1690 (1) Reich, Salzmann, Kawa, *Bull. soc. chim.* (4) **21**, 217–225 (1917). (2) Geigy and Co., Ger. 199,943, July 4, 1908; *Cent.* **1908**, II 363–364; [*C.A.* **2**, 3000 (1908)]. (3) Lock, *Ber.* **66**, 1530 (1933). (4) Olivier, Weber, *Rec. trav. chim.* **52**, 169–174 (1933). (5) Olivier, Weber, *Rec. trav. chim.* **53**, 882 (1934). (6) Lock, *Ber.* **72**, 303 (1939). (7) Hans (to I.G.), Ger. 506,438, Sept. 4, 1930; *Cent.* **1930**, II 3850; *C.A.* **25**, 304 (1931). (8) Dilthey, Quint, Heinen, *J. prakt. Chem.* (2) **152**, 68–72 (1939). (9) Lock, Asinger, *Monatsh.* **59**, 157 (1932). (10) Meisenheimer, Theilacker, Beisswenger, *Ann.* **495**, 254 (1932).

(11) Lock, *Ber.* **66**, 1530 (1933). (12) Böck, Lock, Schmidt, *Monatsh.* **64**, 401–402, 407–408 (1934). (13) Willstädt, *Ber.* **64**, 2692 (1931). (14) Lock, Böck, *Ber.* **70**, 921 (1937). (15) ... Overberger, Allen, Johnston, Clark, *Chem. & Eng. News*

3:1700 1-CHLORONAPHTHOL-2



$C_{10}H_7OCl$

Beil. VI - 648
VI_1—
VI_2-(603)

M.P.	72°	(1)
	71°	(2)
	70–71°	(3)
	70°	(4) (11) (20) (27)
	68–69°	(5)
	68°	(8)

Ndls. from hot aq., ndls. from lgr., pr. from $CHCl_3$; eas. sol. alc., AcOH, C_6H_6, $CHCl_3$, boilg. lgr. — For crystallographic constants see (4). — Volatile with steam.

[For prepn. of C̄ from β-naphthol (1:1540) with Cl_2 in AcOH (80% yield (21)) (3) (4) (6), with SO_2Cl_2 in CS_2 (7) or with $C_6H_5ICl_2$ (84% yield (2)) see indic. refs.; from sodium β-naphtholate in CS_2 suspension on treatment with Cl_2 (8) or in cold aq. with NaOCl (84% yield (5)) (9) see indic. refs.; for formn. of C̄ from β-naphthol (1:1540) as by-prod. of its

oxidn. with $FeCl_3$ to β-dinaphthol (2,2'-dihydroxybinaphthyl-1,1') see (10) (11) (the proportion of C̄ increases with increasing acidity (11)); for formn. of C̄ from β-naphthol as by-prod. of react. with $SeOCl_2$ see (20)]

C̄ with 1 mole Cl_2 in AcOH soln. gives (12) 1,6-dichloronaphthol-2 (3:3600), m.p. 119.5° (12); C̄ with 1 mole Br_2 yields (7) (13) 6-bromo-2-chloronaphthol-2 [Beil. VI-651], ndls. from AcOH with 1 mole solvent, m.p. 92°, anhydrous ndls. by sublimation, m.p. 101° (7). [Note, however, that *C̄ in AcOH + NaOAc with 1 mole Br_2 yields (1)* "1-bromo-1-chloro-2-oxonaphthalenedihydride-1,2," pale yel. pr. from lgr., m.p. 90° when pure but on short stdg. soon becoming lower]

[C̄ in AcOH with conc. HI ($D = 1.5$) boiled 5 hrs gives (79% yield (5)) β-naphthol (1:1540), m.p. 121° (5); note, however, that C̄ is unaffected by $SnCl_2$ either in acid or alk. even after protracted refluxing, but in AcOH/HCl in s.t. 8 hrs. at 100° (1) reduces to β-naphthol]

[C̄ in alk. soln. treated with *p*-nitrobenzenediazonium chloride soln loses its halogen atom and yields (14) (15) (16) cf. (21) 1-(*p*-nitrobenzeneazo)naphthol-2 ("Para Red") [Beil. XVI-165, XVI_1-(255)], red ndls from pyridine, m.p. 246–247° u.c. (14), from AcOH, m.p. 250° cor. (15). (Note, however, that as much as 40% of a light yel. by-prod., m.p. 125° dec., is also formed (16))]

[C̄ melted with PCl_5 and then treated with aq. (4), or C̄ in alk. soln shaken with $POCl_3$ (17), or sodium salt of C̄ shaken in xylene with $POCl_3$ (18), yields *tris*-(1-chloronaphthyl-2) phosphate, ndls from alc., m.p. 152° (4) (note that by the second method (above) *bis*-(1-chloronaphthyl-2)phosphoric acid, ndls. from alc. + HCl, m.p. 251° (4), is also formed (4)).]

[C̄ (2 moles) with Na_2S (1 mole) htd. in aq. under N_2 gives (97.5% yield (19)) *bis*-(2-hydroxynaphthyl-1) sulfide [Beil. VI-976, VI_1-(470)], colorless cryst. from AcOH, m.p. 226° cor. (19).]

C̄ under many circumstances yields ethers with difficulty and small yields; e.g., C̄ with MeOH + conc. H_2SO_4 (25) or *p*-toluenesulfonic acid (26) gives only 2–7% methyl ether; however, C̄ in MeOH/KOH htd. with MeI in s.t. at 100° for 5 hrs. (25), or C̄ in 15% KOH shaken with Me_2SO_4 for ½ hr. (91% yield (5)), gives 1-chloro-2-methoxynaphthalene, pr. from alc., m.p. 70–71° (5), 68° (25), 78° (27); this methyl ether on protracted htg. with conc. HCl in s.t. at 200–250° yields C̄ + MeCl (17) (27). — C̄ with EtOH + conc. H_2SO_4 (25) gives only 0.5–10% ethyl ether, but C̄ with EtOH/KOH + EtBr htd. 3 hrs. at 100° (25) gives 1-chloro-2-ethoxynaphthalene, lfts. from alc., m.p. 58° (25).

Ⓓ **1-Chloro-2-naphthyl acetate:** tbls. from alc., m.p. 42–43° (3). [From C̄ with AcCl (3).]

Ⓓ **1-Chloro-2-naphthyl benzoate:** lfts. from alc., m.p. 101° (27). [From C̄ in alk. soln by shaking with BzCl (27)]

3:1700 (1) Fries, Schimmelschmidt, *Ann.* **484**, 293, 296–297 (1930) (2) Neu, *Ber.* **72**, 1511 (1939) (3) Zincke, *Ber* **21**, 3384–3385 (1888). (4) Cleve, *Ber.* **21**, 895–896 (1888). (5) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 379–380 (1921/22). (6) Clifford (to Goodyear Tire and Rubber Co.), Brit 302,147, Feb. 6, 1929, *Cent* **1929**, I 1867. (7) Armstrong, Rossiter, *Chem. News* **59**, 225 (1889) *Ber* **24**, Referate, 705 (1891). (8) Schall, *Ber.* **16**, 1901 (1883). (9) Kalle and Co., Ger. 168,824, March 16, 1906, *Cent.* **1906**, I 1307. (10) Ioffe, *J. Gen. Chem. (U.S.S.R.)* **7**, 2715–2718 (1937), *Cent* **1939**, II 4475, *C.A.* **32**, 2931 (1938).
(11) Ioffe, Kuznetzov, Litovskii, *J. Gen. Chem. (U.S.S.R.)* **5**, 1655–1656 (1935); *Cent.* **1937**,

m.p. 34–35°, b.p. 137–138° at 17 mm., 134–136° at 13 mm. (corresp. benzoate, m.p. 77°); C̄ with C_6H_5MgBr similarly gives in good yield (1) 2,6-dichlorophenyl-phenyl-carbinol, m.p. 57° (corresp. acetate, m.p. 105°)]. [For conversion of C̄ to 2,6-dichlorostyrene (16) (17) via formn. of 2,6-dichlorophenyl-methyl-carbinol (above) and dehydration of latter with $KHSO_4$ (31.5% yield (16)) see indic. refs.]

C̄ with aniline readily condenses yielding (1) 2,6-dichlorobenzaldehyde anil, m.p. 64–65°.

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—— **2,6-Dichlorobenzaldehyde o-nitrophenylhydrazone:** m.p. 154° (1).

—— **2,6-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.

—— **2,6-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unreported.

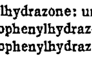
—— **2,6-Dichlorobenzaldehyde *p*-bromophenylhydrazone:** m.p. 142° (1).

—— **2,6-Dichlorobenzaldehyde semicarbazone:** unreported.

3:1690 (1) Reich, Salzmann, Kawa, *Bull. soc. chim.* (4) **21**, 217–225 (1917). (2) Geigy and Co., Ger. 199,943, July 4, 1908; *Cent.* **1908**, II 363–364; [*C.A.* **2**, 3000 (1908)]. (3) Lock, *Ber.* **66**, 1530 (1933). (4) Olivier, Weber, *Rec. trav. chim.* **52**, 169–174 (1933). (5) Olivier, Weber, *Rec. trav. chim.* **53**, 882 (1934). [illegible] Sept. 4, 1930; *Cent.* **1930**, II 3[illegible] *Chem.* (2) **152**, 68–72 (1939). [illegible] Theilacker, Beisswenger, *Ann.* **495**, 254 (1932).

(11) Lock, *Ber.* **66**, 1530 (1933). (12) Bock, Lock, Schmidt, *Monatsh.* **64**, 401–402, 407–408 (1934). (13) Willstädt, *Ber.* **64**, 2692 (1931). (14) Lock, Böck, *Ber.* **70**, 921 (1937). (15) Norris, Klemka, *J. Am. Chem. Soc.* **62**, 1433 (1940). (16) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 863 (1946). (17) Michalek, Clark, *Chem. & Eng. News* **22**, 1559–1563 (1945). (18) Lock, Stach, *Ber.* **76**, 1252–1256 (1943).

3:1700 1-CHLORONAPHTHOL-2



$C_{10}H_7OCl$

Beil. VI - 648
VI_1—
VI_2-(603)

M.P.	72°	(1)
	71°	(2)
	70–71°	(3)
	70°	(4) (11) (20) (27)
	68–69°	(5)
	68°	(8)

Ndls. from hot aq., ndls. from lgr., pr. from $CHCl_3$; eas. sol. alc., AcOH, C_6H_6, $CHCl_3$, boilg. lgr. — For crystallographic constants see (4). — Volatile with steam.

[For prepn. of C̄ from β-naphthol (1:1540) with Cl_2 i[illegible] with SO_2Cl_2 in CS_2 (7) or with $C_6H_5ICl_2$ (84% yield [illegible] naphtholate in CS_2 suspension on treatment with Cl_2 [illegible] yield (5)) (9) see indic. refs.; for formn. of C̄ from β-naphthol (1:1540) as by-prod. of its

oxidn. with $FeCl_3$ to β-dinaphthol (2,2′-dihydroxybinaphthyl-1,1′) see (10) (11) (the proportion of C̄ increases with increasing acidity (11)); for formn. of C̄ from β-naphthol as by-prod. of react. with $SeOCl_2$ see (20).]

C̄ with 1 mole Cl_2 in AcOH soln. gives (12) 1,6-dichloronaphthol-2 (3:3600), m.p. 119.5° (12); C̄ with 1 mole Br_2 yields (7) (13) 6-bromo-2-chloronaphthol-2 [Beil. VI-651], ndls. from AcOH with 1 mole solvent, m.p. 92°, anhydrous ndls. by sublimation, m.p. 101° (7). [Note, however, that C̄ in AcOH + NaOAc with 1 mole Br_2 yields (1) "1-bromo-1-chloro-2-oxonaphthalenedihydride-1,2," pale yel. pr. from lgr., m.p. 90° when pure but on short stdg. soon becoming lower.]

[C̄ in AcOH with conc. HI ($D = 1.5$) boiled 5 hrs. gives (79% yield (5)) β-naphthol (1:1540), m.p. 121° (5); note, however, that C̄ is unaffected by $SnCl_2$ either in acid or alk. even after protracted refluxing, but in AcOH/HCl in s.t. 8 hrs. at 100° (1) reduces to β-naphthol.]

[C̄ in alk. soln. treated with p-nitrobenzenediazonium chloride soln. loses its halogen atom and yields (14) (15) (16) cf. (21) 1-(p-nitrobenzeneazo)naphthol-2 ("Para Red") [Beil. XVI-165, XVI_1-(255)], red ndls. from pyridine, m.p. 246–247° u.c. (14), from AcOH, m.p. 250° cor. (15) (Note, however, that as much as 40% of a light yel. by-prod., m.p. 125° dec., is also formed (16).)]

[C̄ melted with PCl_5 and then treated with aq. (4), or C̄ in alk. soln. shaken with $POCl_3$ (17), or sodium salt of C̄ shaken in xylene with $POCl_3$ (18), yields *tris*-(1-chloronaphthyl-2) phosphate, ndls. from alc., m.p. 152° (4) (note that by the second method (above) *bis*-(1-chloronaphthyl-2)phosphoric acid, ndls. from alc. + HCl, m.p. 251° (4), is also formed (4)).]

[C̄ (2 moles) with Na_2S (1 mole) htd. in aq. under N_2 gives (97.5% yield (19)) *bis*-(2-hydroxynaphthyl-1) sulfide [Beil. VI-976, VI_1-(470)], colorless cryst. from AcOH, m.p. 226° cor. (19).]

[C̄ on refluxing a few hrs. with aniline (best under N_2 (23)) yields (22) 1-anilinonaphthol-2 [Beil. XIII-678], ndls. from lgr., m.p. 153–154° (22), 155–156° (23); for corresp. reactn. with many other monamines (22) (23) and diamines (24) see indic. refs.]

C̄ under many circumstances yields ethers with difficulty and small yields; e.g., C̄ with MeOH + conc. H_2SO_4 (25) or p-toluenesulfonic acid (26) gives only 2–7% methyl ether; however, C̄ in MeOH/KOH htd. with MeI in s.t. at 100° for 5 hrs. (25), or C̄ in 15% KOH shaken with Me_2SO_4 for ½ hr. (91% yield (5)), gives 1-chloro-2-methoxynaphthalene, pr. from alc., m.p. 70–71° (5), 68° (25), 78° (27); this methyl ether on protracted htg. with conc. HCl in s.t. at 200–250° yields C̄ + MeCl (17) (27). — C̄ with EtOH + conc. H_2SO_4 (25) gives only 0.5–10% ethyl ether, but C̄ with EtOH/KOH + EtBr htd. 3 hrs. at 100° (25) gives 1-chloro-2-ethoxynaphthalene, lfts. from alc., m.p. 58° (25).

Ⓓ **1-Chloro-2-naphthyl acetate**: tbls. from alc., m.p. 42–43° (3). [From C̄ with AcCl (3).]

Ⓓ **1-Chloro-2-naphthyl benzoate**: lfts. from alc., m.p. 101° (27). [From C̄ in alk. soln. by shaking with BzCl (27).]

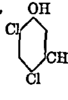
3:1700 (1) Fries, Schimmelschmidt, *Ann.* **484**, 293, 296–297 (1930). (2) Neu, *Ber.* **72**, 1511 (1939). (3) Zincke, *Ber.* **21**, 3384–3385 (1888). (4) Cleve, *Ber.* **21**, 895–896 (1888). (5) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 379–380 (1921/22). (6) Clifford (to Goodyear Tire and Rubber Co.), Brit. 302,147, Feb. 6, 1929, *Cent.* **1929**, I 1867. (7) Armstrong, Rossiter, *Chem. News* **59**, 225 (1889), *Ber.* **24**, Referate, 705 (1891). (8) Schall, *Ber.* **16**, 1901 (1883). (9) Kalle and Co., Ger. 168,824, March 16, 1906, *Cent.* **1906**, I 1307. (10) Ioffe, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 2715–2718 (1937), *Cent.* **1939**, II 4475; *C.A.* **32**, 2931 (1938).

(11) Ioffe, Kuznetzov, Litovskii, *J. Gen. Chem.* (*U.S.S.R.*) **5**, 1685–1686 (1935); *Cent.* **1937**,

[illegible]
fabrikation, Ger. 246,871, May 11, 1912; *Cent.* **1912**, I 1875. (19) Ringeissen, *Compt. rend.* **198**, 2182 (1934); *Cent.* **1934**, II 2677; *C.A.* **28**, 5432. (20) Morgan, Burstall, *J. Chem. Soc.* **1928**, 3269.
(21) Pollak, Gebauer-Fülnegg, *Monatsh.* **50**, 317 (1928). (22) Wahl, Lantz, Ger. 365,367, [illegible]

34–37 (1895).

3:1745 4,6-DICHLORO-3-METHYLPHENOL $C_7H_6OCl_2$ **Beil. S.N. 526**
(4,6-Dichloro-*m*-cresol)



M.P. 71.5–72° (1) **B.P. 235–236° (1)**

C̄ is volatile with steam. — The products of m.p. 45–46° (2) and m.p. 58° (3) formerly supposed to have been C̄ are now regarded (1) as 2,4,6-trichloro-3-methylphenol (3:0618) and 2,4-dichloro-3-methylphenol (3:1205) respectively.

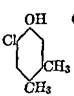
[For prepn. of C̄ from 6-amino-4-chloro-3-methylphenol (1) via diazotization and use of Cu_2Cl_2 reaction see (1); from 4,6-diamino-3-methylphenol (1) via tetrazotization and use of Cu_2Cl_2 reaction see (1); for formn. of C̄ (together with other isomers) from 4-chloro-3-methylphenol (3:1535) or from 6-chloro-3-methylphenol (3:0700) in $CHCl_3$ with Cl_2 (1 mole) see (1).]

C̄ in $CHCl_3$ with 1 mole Cl_2 gives alm. quant. yields (1) 2,4,6-trichloro-3-methylphenol (3:0618), m.p. 46° (1).

- Ⓓ **4,6-Dichloro-3-methylphenyl benzoate:** mats of very fine ndls. from alc., m.p. 57.5° (1). [From C̄ with BzCl in pyridine (1).]
- Ⓓ **4,6-Dichloro-3-methylphenyl benzenesulfonate:** thin lustrous plates from alc., m.p. 86° (1). [From C̄ + benzenesulfonyl chloride in pyridine (1).]
- Ⓓ **4,6-Dichloro-3-methylphenyl *p*-toluenesulfonate:** very fine ndls. from alc., m.p. 104–105° (1). [From C̄ + *p*-toluenesulfonyl chloride in pyridine (1).]

3:1745 (1) Huston, Chen, *J. Am. Chem. Soc.* **55**, 4216–4218 (1933). (2) von Walther, Zipper, *J. prakt. Chem.* (2) **91**, 374 (1864). (3) Tanaka, Morikowa, Sakamoto, *J. Chem. Soc. Japan* **51**, 275–277 (1930), *C.A.* **26**, 706–707 (1932).

3:1754 6-CHLORO-3,4-DIMETHYLPHENOL C_8H_9OCl **Beil. VI —**
(5-Chloro-*o*-4-xylenol) **VI_1—**
VI_2-(456)



M.P. 71.5–72.5° (1)
72° (2)
71° (4)

Ndls. from lt. pet. — Volatile with steam.

[For prepn. of C̄ from 6-amino-3,4-dimethylphenol (5-amino-o-4-xylenol) [Beil. XIII-629, XIII$_1$-(244)] (1) via diazotization and use of Cu_2Cl_2 reaction (yield not stated) see (1); from 3,4-dimethylphenol (o-4-xylenol) (1:1453) with SO_2Cl_2 in $CHCl_3$ (23% yield) see (4) cf. (2) (3).]

[For studies on bactericidal action of C̄ see (2) (3).]

C̄ with Cl_2 does *not* (1) give a trichloro derivative.

C̄ with HNO_3 in AcOH soln. as directed gives (5) 2-nitro-6-chloro-3,4-dimethylphenol (5-chloro-3-nitro-o-4-xylenol), yel. pl from C_6H_6, m.p. 127.5° (5); note, however, that neither the isomeric mononitro deriv. nor the corresp dinitro deriv. is known.

C̄ does *not* (5) couple with benzenediazonium chloride.

[For behavior of C̄ with sulfur chloride + $AlCl_3$ in CS_2 see (6).]

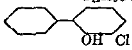
—— **6-Chloro-3,4-dimethylphenyl acetate:** unreported.

Ⓓ **6-Chloro-3,4-dimethylphenyl benzoate:** m p. 43° (1).

3:1754 (1) Hinkel, Collins, Ayling, *J. Chem Soc* **123**, 2973 (1923) (2) Heicken, *Angew. Chem.* **52**, 263–265 (1939). (3) Lockemann, Kunzmann, *Angew. Chem.* **46**, 296–301 (1933). (4) McClement, Smiles, *J. Chem. Soc* **1937**, 1019 (5) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 2530–2531. (6) Dvorkovitz, Smiles, *J. Chem. Soc.* **1938**, 2026.

3:1757 6-CHLORO-2-PHENYLPHENOL $C_{12}H_9OCl$ **Beil. S.N. 539**

(3-Chloro-2-hydroxybiphenyl; "o-chloro-o′-phenylphenol")



M.P.	**73–74°** (1)	**B.P. 312°**	at 745 mm.	(4)
	72° (4)	**172°**	at 15 mm.	(4)
	71–72° (3) (6)	**137–138°**	at 5 mm.	(6)
		138–140°	at 3 mm.	(10)

[*See also 4-chloro-2-phenylphenol* (3:8980).]

Important Note. Through the year 1944 (and perhaps in some cases beyond) the chlorophenylphenol of m.p. 72° (C̄) has been regarded as having the structure 4-chloro-2-phenylphenol = 5-chloro-2-hydroxybiphenyl = "p-chloro-o-phenylphenol." In 1945, however, this view was corrected by the paper of Weissberger and Salminen (1); in this text, therefore, expression of the facts is reported in the light of their paper. Particular care is, therefore, required in consulting reference prior to it since such material is universally expressed in the reverse sense of the present view.

[For prepn. of C̄ from 2-hydroxybiphenyl (1:1440) with Cl_2 (note that 4-chloro-2-phenylphenol (3:8980) is also formed) see (2) (4); for prepn. of C̄ from 3-amino-2-hydroxybiphenyl (5) by diazotization and use of Cu_2Cl_2 reaction (45% yield (1)) see indic. refs]

C̄ is sol. in aq 25% NaOH at 60°, but resultant salt is more sol than corresp. prod. from the isomeric 4-chloro-2-phenylphenol (3:8980) (for use in sepn of C̄ from the latter see (4)); note that sodium salt of C̄ cryst. as trihydrate, i.e., NaĀ.3H_2O (4), and that anhydrous NaĀ dec. at 316° without melting (4).

The calcium salt of C̄ is very spar. sol. aq. (use in sepn. of C̄ from the isomeric 4-chloro-2-phenylphenol (3)).

[For reaction of $\bar{C}$ with methallyl chloride (3:7145) in pres. of alk. see (10).]

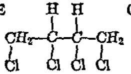
$\bar{C}$ on mononitration with HNO_3 in AcOH at 15–19° as directed gives (31% *yield* (1)) 3-chloro-2-hydroxy-5-nitrobiphenyl, tan needles, m.p. 130–131° (1), 129–131° (6).

[$\bar{C}$ (?) on condensation with formaldehyde + ethanolamine as directed (9) *gives a prod.*, m.p. 182–183°; for similar condens. of $\bar{C}$ (?) with formaldehyde + *morpholine* see (7).]

—— 6-Chloro-2-phenylphenyl benzoate: m.p. 88.5° (8). [Note that this prod. does *not* distinguish $\bar{C}$ from the isomeric 4-chloro-2-phenylphenol (3:8980), whose benzoate has m.p. 86–87°.]

3:1757 (1) Weissberger, Salminen, *J. Am. Chem. Soc.* **67**, 58–60 (1945). (2) Britton, Bryner (to Dow Chem. Co.), U.S. 1,969,963, Aug. 14, 1934; *C.A.* **28**, 6160 (1934). (3) Rittler, Heller (to Chem. Fabrik von Heyden) ...
(1935). (4) Britton, Bry...
I 128–129; *C.A.* **27**, 5086...
578 (1934). (5) Vorozhts...
1940, II 2152; *C.A.* **32**, 79...
59–64 (1939); *Cent.* **1940**, 2...
U.S. 2,040,039, May 5, 193...
tiansen, *J. Am. Pharm. Assoc.* **24**, 553–557 (1935). (9) Bruson, *J. Am. Chem. Soc.* **58**, 1743 (1936). (10) Coleman, Moore (to Dow Chem. Co.), U.S. 2,170,990, Aug. 29, 1939; *Cent.* **1939**, II 4592; *C.A.* **34**, 1098 (1940).

3:1760 1,2,3,4-TETRACHLOROBUTANE (solid isomer) (Butadiene tetrachloride; erythrene tetrachloride)



$C_4H_6Cl_4$ Beil. I - 119 I_1-(38) I_2—

M.P. 73–74° (1) (2); 72.5–73° (3); 72° (4); 70° (5)

B.P. 130–134° at 40 mm. (4)

This compd. is known in two diastereoisomeric forms, one solid ($\bar{C}$), and one liquid (3:9082) q.v.

$\bar{C}$ cryst. from alc. (1) or CCl_4 (3) in colorless pr. with strong camphoraceous odor.

[For preparation of $\bar{C}$ from butadiene-1,3 by treatment in cold with Cl_2 (4) (6) (7) in CS_2, CCl_4, $CHCl_3$, or lgr. soln. (4), or with SCl_2 in pet. ether (1) see indic. refs.; for prepn. from 1,2,3,4-tetrahydroxybutane (erythritol) (1:5825) with PCl_5 in CS_2 see (3); for formn. from acetylene + HCl in electric discharge see (2).] [The proportion of solid ($\bar{C}$) and liq. (3:9082) isomers formed varies with conditions.]

$\bar{C}$ on warming with Zn dust in alc. yields (4) butadiene-1,3, b.p. −4.8°.

$\bar{C}$ with MeOH/KOH at 10–18° loses 2 HCl yielding (8) 2,3-dichlorobutadiene-1,3 (3:5220), b.p. 39–40° at 80 mm., and other products.

3:1760 (1) Backer, Strating, *Rec. trav. chim.* **54**, 55–56 (1935). (2) Losanitch, *Cent.* **1913**, II 754.

3:1775 3,4-DIMETHYLPHENACYL CHLORIDE $C_{10}H_{11}OCl$ Beil. VII - 323
(ω-Chloro-3,4-dimethyl-acetophenone) VII$_1$-(172)

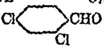
M.P. 73°

[For prepn. from *o*-xylene (1:7430) + chloroacetyl chloride (3:5235) + $AlCl_3$ see (1) (2).]

C̄ on oxidn. with alk. $KMnO_4$ gives 4-methylisophthalic ac. [Beil. IX-863], m.p. 332° cor. (corresp. dimethyl ester, ndls. from MeOH, m.p. 80°).

3:1775 (1) Kunckell, *Ber.* **30**, 1713 (1897). (2) Jörlander, *Ber.* **50**, 1459 (1917).

3:1800 2,4-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII - 236
VII$_1$-(134)



M.P. 74.5° (1)
72° (2)
71 (3) (5)
70–71° (4)

White ndls. with strong odor like ordinary benzaldehyde. — Volatile with steam (1).

[For prepn. of C̄ from 2,4-dichlorotoluene (3:6290) via bromination at 180–200° to 2,4-dichlorobenzal (di)bromide and hydrolysis with conc. H_2SO_4 at 100° (92% yield) see (1); for analogous prepn. via 2,4-dichlorobenzal (di)chloride and its hydrolysis see (2) (4); for prepn. of C̄ from 2-chloro-4-aminobenzaldehyde via diazo/CuCl reactn. see (3).]

C̄ on oxidn. with $KMnO_4$ yields 2,4-dichlorobenzoic acid (3:4560), m.p. 162°. — C̄ on htg. with MeOH/NaOMe in s.t. at 183° for 8 hrs. undergoes Cannizzaro reactn. yielding 2,4-dichlorobenzyl alc., m.p. 58–59° (2), and 2,4-dichlorobenzoic ac. (3:4560), m.p. 161–162° (2).

C̄ on mononitration as specified (6) yields 2,4-dichloro-6-nitrobenzaldehyde [Beil. VII-263], cryst. from lgr., m.p. 74–75° (6). [Note that 2,4-dichloro-5-nitrobenzaldehyde [Beil. VII$_1$-(144)], m.p. 74°, has also been prepd. indirectly.]

[For conversion of C̄ to 2,4-dichlorostyrene (7) (8) via reaction with MeMgI giving (63% yield (1)) 2,4-dichlorophenyl-methyl-carbinol, b.p. 130–134° at 11 mm. (1), 127° at 7 mm. (corresp. *p*-nitrobenzoate, m.p. 113° (1)), and dehydration of latter with $KHSO_4$ (33% yield (7)) see indic. refs.]

Ⓓ **2,4-Dichlorobenzaldoxime:** ndls., m.p. 136–137° (4). [The oxime hydrochloride has m.p. 133.5° but on treatment with Na_2CO_3 yields oxime (4).]

—— **2,4-Dichlorobenzaldehyde phenylhydrazone:** unrecorded.

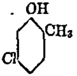
—— **2,4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone:** unrecorded.

—— **2,4-Dichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.

—— **2,4-Dichlorobenzaldehyde semicarbazone:** unrecorded.

3:1800 (1) Lock, Böck, *Ber.* **70**, 923 (1937). (2) van der Lande, *Rec. trav. chim.* **51**, 103, 109 (1932). (3) Blanksma, *Chem. Weekblad* **6**, 899–913 (1909), *Cent.* **1910**, I 261. (4) Erdmann, Schwechten, *Ann.* **260**, 68–69 (1890). (5) Seelig, *Ann.* **237**, 169 (1887). (6) Geigy and Co., Ger. 198,909; *Cent.* **1908**, II 214. (7) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 862–863 (1946). (8) Michalek, Clark, *Chem. & Eng. News* **22**, 1559–1563 (1945).

3:1815 5-CHLORO-2-METHYLPHENOL (5-Chloro-o-cresol)



C_7H_7OCl Beil. VI — VI_1-(174) VI_2-(332)

M.P. 73–74° (1) (4)

Long white hard ndls. from pet. eth.; eas. sol. alc., AcOH; less sol. pet. eth. (1).

C̄ is eas. sol. alk. (1).

[For prepn. from 5-chloro-2-methylaniline [Beil. XII-835] see (1) (4).]

C̄ on mononitration (2) in AcOH with fumg. HNO_3 at 5° gives mixt. of two mononitration products: 6-nitro-5-chloro-2-methylphenol, volatile with steam, golden-yel. pr. from pet. eth., m.p. 54.5–55° (2), and 4-nitro-5-chloro-2-methylphenol, not volatile with steam, cryst. from aq. or C_6H_6, m.p. 144–145° (2).

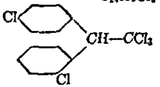
C̄ on nitration (3) with 3 pts. HNO_3 ($D = 1.48$) at 0° gives a dinitro compd., 4,6-dinitro-*5-chloro-2-methylphenol [Beil. VI_1-(181)]*, yel. ndls., from pet. eth., m.p. 146° (3); acetyl deriv., m.p. 109–110° (3).

[For action of HNO_2 on C̄ see (4).]

Ⓓ 5-Chloro-2-methylphenyl benzoate: from C̄ + BzCl + aq. alk., white lfts. from alc., m.p. 53–54° (1).

3:1815 (1) Zincke, *Ann.* **417**, 207–208 (1918). (2) von Auwers, Schornstein, *Cent.* **1924**, II 2269. (3) Zincke, *Ann.* **418**, 234 (1918). (4) Hodgson, Moore, *J. Chem. Soc.* **1926**, 2037.

3:1820 1,1,1-TRICHLORO-2-(o-CHLOROPHENYL)-2-(p-CHLOROPHENYL)ETHANE ("o,p′-DDT")



$C_{14}H_9Cl_5$ Beil. S.N. 479

M.P. 74.0–74.5° (4) cor. (6)
73–74° (5)

This compound is the so-called *o,p*-isomer of "DDT" (3:3298). Although known to be a substantial contaminant (e.g., 18% (1) –19% (5)) of technical "DDT," very little information is at present available regarding it.

Cryst. from MeOH.

[For prepn. of C̄ from 2,2,2-trichloro-1-(o-chlorophenyl)ethanol (5) with chlorobenzene (3:7903) in pres. of conc. H_2SO_4 at 60° (64% yield) see (5).]

C̄ on dinitration with fumg. HNO_3 at 50° for 1 hr. gives (5) a dinitro deriv., cryst. from 95% alc., m.p. 148.0–148.5° cor. (5); note that this prod. has same m.p. as corresp. deriv. from "DDT" but that m.p. of a mixt. of the two dinitro compds. is depressed.

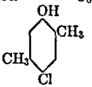
C̄ on tetranitration with a mixt. (1:1 by volume) of fumg. HNO_3 + conc. H_2SO_4 at 100° for 1 hr. gives (2) a prod., m.p. 229.5–230° cor.; note that the corresp. prod. from "DDT" has m.p. 223.5–224.5° cor. (2).

C̄ with anhydrous $AlCl_3$ (1 mole) + large excess C_6H_6 at ord. temp. evolves HCl and gives (10% yield (3)) 1,1,2,2-tetraphenylethane, m.p. 211°; *in this connection see corresp.* behavior of "DDT" (3:3298).

C̄ with alc. KOH loses 1 HCl giving (97% yield (5)) (7) 1,1-dichloro-2-(o-chlorophenyl)-2-*(p-chlorophenyl)ethylene (3:1025), accompanied* by a little *o,p′*-dichlorodiphenylacetic acid, m.p. 106–107.5° cor. (7), the proportion of which may be increased by reaction of C̄ with $Ba(OH)_2$ in ethylene glycol at 175° (7).

3:1820 (1) Gunther, *J. Chem. Education* **22**, 239 (1945). (2) Schechter, Haller, *J. Am. Chem. Soc.* **66**, 2129–2130 (1944). (3) Fleck, Preston, Haller, *J. Am. Chem. Soc.* **67**, 1419–1420 (1945). (4) Cristol, Hayes, Haller, *Ind. Eng. Chem., Anal. Ed.* **17**, 470–473 (1945). (5) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1591–1602 (1945). (6) Cristol, *J. Am. Chem. Soc.* **67**, 1498 (1945). (7) Cristol, Haller, *J. Am. Chem. Soc.* **67**, 2222–2223 (1945).

3:1822 4-CHLORO-2,5-DIMETHYLPHENOL C_8H_9OCl Beil. VI —
(5-Chloro-*p*-2-xylenol) VI_1—
VI_2-(467)



M.P. 74–75° (1)
74° (2)

Ndls. from lgr.

[For prepn. of $\bar{C}$ from 2,5-dimethylphenol (*p*-xylenol) (1:1473) by chlorination with $SOCl_2$ in $CHCl_3$ (1) or AcOH (2) see indic. refs.]

[For studies of bactericidal action of $\bar{C}$ see (2) (3).]

[For behavior of $\bar{C}$ with *o*-nitrosulfenyl chloride see (4) cf. (5); behavior of $\bar{C}$ with sulfur chloride in CS_2 see (1).]

—— 4-Chloro-2,5-dimethylphenyl acetate: unreported.
—— 4-Chloro-2,5-dimethylphenyl benzoate: unreported.

3:1822 (1) Lesser, Gad, *Ber.* **56**, 977 (1923). (2) Heicken, *Angew. Chem.* **52**, 264–265 (1939). (3) Lockemann, Kunzmann, *Angew. Chem* **46**, 296–301 (1933). (4) Learmonth, Smiles, *J. Chem. Soc.* **1936**, 327–328. (5) McClement, Smiles, *J. Chem. Soc.* **1937**, 1019–1021.

3:1831 α,α,γ-TRICHLORO-*n*-BUTYRIC ACID $C_4H_5O_2Cl_3$ Beil. II-281
II_1—
II_2—

Cl
$CH_2.CH_2.C.COOH$
Cl Cl

M.P. 73–75° (1)

Cryst. with sharp odor suggesting chloroacetic acid. — Sol. in 20 pts. aq. — $\bar{C}$ blisters skin. — $\bar{C}$ in small amts. (5 g.) can (with care) be distilled, but attempts to distil larger units lead to decomposition with loss of HCl (2).

[For prepn. of $\bar{C}$ from α,α,γ-trichloro-*n*-butyraldehyde (3:9094) by odixn. with fumg. HNO_3 in cold see (1).]

$\bar{C}$ does not react with Zn dust in aq. or with aq. KI even at 100° (2); $\bar{C}$ does not react with NH_2OH (2).

$\bar{C}$ on boilg. with aq. (100 pts.) for 4 days yields (2) a soln. which is strongly acid, reduces Fehling soln. and hot $NH_4OH/AgNO_3$, and presumably conts. $HOCH_2$ $CH_2.CO.COOH$.

$\bar{C}$ with aq. Na_2CO_3 loses one of its three chlorine atoms (probably that in γ position) and upon acidification gives a soln. presumably contg. a lactone; for details see (2).

The acid chloride corresp. to $\bar{C}$ is unreported.

—— Methyl α,α,γ-trichloro-*n*-butyrate: unreported.
—— Ethyl α,α,γ-trichloro-*n*-butyrate: unreported.
—— α,α,γ-Trichloro-*n*-butyramide: unreported.
—— α,α,γ-Trichloro-*n*-butyranilide: unreported.
—— α,α,γ-Trichloro-*n*-butyr-α-naphthalide: unreported.

3:1831 (1) Natterer, *Monatsh.* **4**, 551–553 (1883). (2) Natterer, *Monatsh.* **5**, 258–265 (1884).

3:1840 α,β,β-TRICHLOROACRYLIC ACID

$$Cl_2C{=}C(Cl){-}COOH$$

$C_3HO_2Cl_3$ Beil. II - 402, II_1-(187), II_2-(388)

M.P. 76° (1) (2) (13)
74–75° (3)
73° (4)
72.9° (5)

B.P. 221–223° at 760 mm. (5)
133° cor. at 30 mm. (5)

Pr. from CS_2 or dry ether. — $\bar{C}$ is very eas. sol. hot aq. but spar. sol. cold aq.; at 25° its satd. aq. soln. conts. 6.4% $\bar{C}$ (1), at 20° 6% $\bar{C}$ (2). — $\bar{C}$ with aq. within certain limits forms two liq. layers; for thermal anal. of the system see (5); note that $\bar{C}$ with aq. forms a compd. of compn. $\bar{C}$ + 2.5 H_2O, m.p. −0.6°, and that $\bar{C}$ with this compound forms a eutectic, m.p. 17° (5). — $\bar{C}$ is very sol. in alc., ether, or $CHCl_3$.

[$\bar{C}$ is usually prepd. from hexachloropropylene (3:6370) by direct or indirect hydrolysis of its terminal —CCl_3 group to —COOH; for prepn. of $\bar{C}$ from hexachloropropylene by such hydrolysis with 90% H_2SO_4 in pres. of $Al_2(SO_4)_3$ at not above 130° (5) (1) cf. (6) (7) (81% yield (13)) or with boilg. aq. susp. of $BaCO_3$ (isolated as $Ba\bar{A}_2$ in 92% yield (1)) see indic. refs.; for prepn. of $\bar{C}$ from hexachloropropylene (3:6370) via conversion with alc. NaOEt to triethyl orthotrichloroacrylate and subsequent quantitative hydrolysis with alc. KOH see (4).]

[For formn. of $\bar{C}$ from hexachlorocyclopentanedione-1,3 [Beil. VII-553] by hydrolytic cleavage with 10% NaOH (3), or from β-bromo-α,β,β-trichloropropionic acid (see below) by elimination of HBr on stdg. several days with aq. $Ba(OH)_2$ (2), see indic. refs.]

$\bar{C}$ on reduction with H_2 in pres. of Pd cat. at ord. temp. and press. absorbs 4 moles H_2 yielding (8) propionic acid (1:1025).

$\bar{C}$ with Cl_2 in CCl_4 soln. in sunlight adds 1 mole halogen giving (9) (8) pentachloropropionic acid (3:4895).

[$\bar{C}$ with HBr might be expected to yield β-bromo-α,β,β-trichloropropionic acid, but this reaction is unreported although the expected prod. [Beil. II-257], m.p. 83–84° has been prepd. by other means and with $Ba(OH)_2$ loses HBr giving $\bar{C}$ (2).]

$\bar{C}$ with half its wt. of PCl_5 at 80° loses H_2O between two molecules giving (4) trichloroacrylic acid anhydride, cryst., insol. aq., m.p. 39–40° (4) (5); this product is also formed during the distillation of $\bar{C}$ even at reduced press. (5).

$\bar{C}$ with excess $SOCl_2$, however, gives (80–90% yield (1)) (13) trichloroacryloyl chloride (3:5845) q.v.

Salts of $\bar{C}$. [$Na\bar{A}$ (conductivity of aq. solns.) (10); $K\bar{A}$, spar. sol. cold aq. (2); $Ag\bar{A}$, spar. sol. cold aq. but recryst. from hot aq. without decompn. (2) (4); $Mg\bar{A}_2.3\frac{1}{2}H_2O$, sol. aq. (10); $Ca\bar{A}_2.3\frac{1}{2}H_2O$, sol. aq. (10) (2); $Sr\bar{A}_2$ $5H_2O$, sol. aq. (10); $Ba\bar{A}_2.3\frac{1}{2}H_2O$, sol. aq. (10) (2) (note that this salt on htg. in atm. of H_2 gives (11) dichloroacetylene (3:5010)); $Zn\bar{A}_2.6H_2O$ and $Zn\bar{A}_2.3\frac{1}{2}H_2O$ (10); $Cd\bar{A}_2.2H_2O$ (10); $Hg\bar{A}_2$ (no crystal aq.) (10).]

—— Methyl α,β,β-trichloroacrylate: unreported.

—— *Ethyl α,β,β-trichloroacrylate: b.p. 192–194°; 112–114° at 50 mm.;* D_4^{20} = 1.2183; n_D^{20} = 1.4649 (4). [Prepd. indirectly from triethyl orthotrichloroacrylate (itself obtd. from hexachloropropylene with NaOEt) by shaking with conc. HCl (4).]

Ⓓ α,β,β-Trichloroacrylamide: m.p. 97° (12), 96–97° (4), 96° (2). [From trichloroacryloyl chloride (3:5845) with conc. NH_4OH (4) or from ethyl trichloroacrylate (above) with alc. NH_3 (12)]

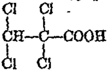
Ⓓ α,β,β-Trichloroacrylanilide: m.p. 98° (13). [From trichloroacryloyl chloride (3:5845) with aniline in $CHCl_3$ at 0° (77% yield) (13).]

3:1840 (1) Böeseken, Dujardin, *Rec. trav. chim.* **32**, 98–101 (1913). (2) Maberry, *Am. Chem. J.* **9**, 3–6 (1887). (3) Zincke, Rohde, *Ann.* **299**, 380 (1898). (4) Fritsch, *Ann.* **297**, 315–318 (1897). (5) Böeseken, Carriere, *Rec. trav. chim.* **34**, 179–186 (1915). (6) Prins, *J. prakt. Chem.* (2) **89**, 416 (1914). (7) Prins, Ger. 261,689, July 2, 1913, *Cent.* **1913**, II 394–395, *C.A.* **7**, 3641 (1913). (8) Böeseken, van der Weide, *Rec. trav. chim.* **35**, 272–273 (1927). (9) Böeseken, *Rec. trav. chim.* **46**, 841 (1927). (10) Böeseken, *Rec. trav. chim.* **46**, 844–846 (1927).

(11) Böeseken, Carriere, *Verslag Akad. Wetenschappen* **22**, 1186–1188 (1914). (12) Gilta, *Bull. soc. chim. Belg.* **39**, 587–588 (1930). (13) Bergmann, Haskelberg, *J. Am. Chem. Soc.* **63**, 1438 (1941).

3:1850 α,α,β,β-TETRACHLOROPROPIONIC ACID

$C_3H_2O_2Cl_4$ Beil. II-253, II₁—, II₂—



M.P. 76° (1)

Colorless cryst. from $CS_2 + CHCl_3$; fairly *sol.* aq.

[For prepn. of C̄ from α,β-dichloroacrylic acid (3:2265) in CS_2 with dry Cl_2 in sunlight see (1).]

Salts: KĀ; AgĀ (readily dec. to AgCl on warming aq. soln.); $Ca\bar{A}_2$; $Ba\bar{A}_2$ (1).

3:1850 (1) Maberry, Smith, *Ber.* **22**, 2659–2660 (1889).

3:1875 β,β-DICHLOROACRYLIC ACID

$C_3H_2O_2Cl_2$ Beil. II-401, II₁—, II₂—

$Cl_2C{=}CH.COOH$

M.P. 76–77° (1) (2) (3)
(*Also see text.*)

Ndls. from pet. ether or by sublimation. — C̄ is spar. sol. aq. but *very eas. sol. ether* or $CHCl_3$. — C̄ on htg. above its m.p. (e.g., to 120°), then rapidly cooled to 60° or below remelts at 63–64° (2) (3); on standing, however, C̄ finally reverts to the form of m.p. 76–77°. — C̄ decomposes on attempted distn.

[For prepn. of C̄ from propiolic acid (acetylene-carboxylic acid) [Beil. II-477] by conversion to chloropropiolic acid (3:1685) and subsequent addn. of 1 HCl by htg. with a large excess conc. HCl at 100° for 5 hrs. (77% overall yield from propiolic acid) see (1); for formn. from "chloralide" (3:3510) by reduction with Zn + HCl in alc. soln. see (2) (3).]

The behavior of C̄ toward hydrogenation has not been reported.

Neither C̄ *nor* its ethyl ester (see below) [illegible]

[C̄ with [illegible]

the formn. [illegible]

tion somet. [illegible]

Salts: KĀ [illegible] $2H_2O$ (2); $Ba\bar{A}_2.2H_2O$ (2); $Zn\bar{A}_2.2H_2O$ (3).

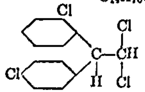
C̄ with PCl_5 gives (3) β,β-dichloroacryloyl chloride, b.p. above 145°; this prod. with EtOH or C̄ in EtOH with dry HCl gives (3) ethyl β,β-dichloroacrylate, b.p. 173–175°.

—— β,β-Dichloroacrylamide: ndls. from $CHCl_3$, m.p. 112–113° (3). [From the above acid chloride with dry NH_3 (3).]

3:1875 (1) Straus, Kollek, Heyn, *Ber.* **63**, 1876–1877 (1930). (2) Wallach, *Ann.* **203**, 83–94 (1880). (3) Wallach, *Ann.* **193**, 6–8, 19–28 (1878).

3:1890 1,1-DICHLORO-2-(*o*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL)ETHANE ("*o,p*-DDD")

$C_{14}H_{10}Cl_4$ Beil. S.N. 474



M.P. 76–78° (1)

Colorless cryst. from MeOH or from pentane. — Note that Č is a minor impurity in technical grade "DDT" (3:3298).

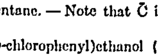
[For prepn. of Č from 2,2-dichloro-1-(*o*-chlorophenyl)ethanol (1) with chlorobenzene (3:7903) in pres. of H_2SO_4 (39% yield) see (1).]

Č with alc. KOH loses 1 HCl giving (1) 1-chloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethylene (not described) which upon oxidn. with CrO_3/AcOH gives (1) 2,4-dichlorobenzophenone (3:1565).

3:1890 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600 (1945).

3:1900 2-CHLORO-4-PHENYLPHENOL (3-Chloro-4-hydroxybiphenyl)

$C_{12}H_9OCl$ Beil. S.N. *539*



M.P. 77° (1) (4) B.P. 176.6° at 5 mm. (5)

Č is sol. in NaOH. [For prepn. of NaĀ using solns. of Č in org. solv. such as MeOH, ether, or toluene see (2).]

Č htd. with NaOH/Na_2CO_3 soln. under press. for 3 hrs. at 290–300° gives 4-phenylpyrocatechol [Beil. VI-990], m.p. 145°; diacetate, m.p. 77.5–78° (3).

Č in CCl_4 stood 5 days with 1 mole Br_2 gave (44% yield) 6-bromo-2-chloro-4-phenylphenol, wh. pr. (from $CHCl_3$), m.p. 84–86° cor. (4); Č in AcOH (25% yield) or in CS_2 (56% yield) stood 2 days with 2 moles Br_2 gave 6-bromo-4′-(*p*-bromophenyl)-2-chlorophenol, coarse wh. ndls., m.p. 143–146° cor. (4).

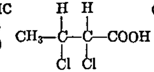
Č in AcOH treated with 1 mole HNO_3 in AcOH gave 38% yield of 2-chloro-6-nitro-4-*phenylphenol, thick yel. pl. (from CCl_4), m.p. 89–90° cor. (5).*

Č with $(CH_3)_2SO_4$ + NaOH (1) or CH_3I + aq. KOH (5) yields the corresp. Me ether, 2-chloro-4-phenylanisole, m.p. 91–92° (1), 93° cor. (5).

- Ⓓ **2-Chloro-4-phenyl-phenyl acetate:** *m.p. 68° (7).* [From Č + Ac_2O + NaOAc in 92% yield (7).]
- Ⓓ **2-Chloro-4-phenyl-phenyl benzoate:** from Č + BzCl + aq. alk. in 80% yield (4); cryst. from AcOH (4), m.p. 95–97° cor. (4), 110–111° (6).
- Ⓓ **2-Chloro-4-phenyl-phenyl benzenesulfonate:** m.p. *59–60° (8). [From Č + benzenesulfonyl chloride* + aq. 10% NaOH (8).]
- Ⓓ **2-Chloro-4-phenyl 2,4-dinitrophenyl ether:** from Č + 2,4-dinitrochlorobenzene in conc. aq. KOH refluxed for several hrs.; yield, 70%; m.p. 109–111°C. (4).

U.S. 1,832,484, Nov. 17, 1931; *Cent.* **1932**, I 740. (2)
Apr. 17, 1934; *Cent.* **1934**, II 1991. (3) Harvey
27, 1934; *Cent.* **1934**, II 1846. (4) Colbert, Meigs,
4). (5) Colbe
J. Am. Pha
Savoy, Abernathy, *J. Am. Chem. Soc.* **64**, 2220 (1942).
Soc. **64**, 2720 (1942).

3:1903 **α,β-DICHLORO-n-BUTYRIC ACID (high-melting isomer)** (Isocrotonic acid dichloride)



$C_4H_6O_2Cl_2$ Beil. II-279, II_1—, II_2—

M.P. 78° (1) (2) (5) **B.P. 131.5°** at 20 mm. (2)
72–73° (3) (4) **130–131°** at 18 mm. (5)

[*See also α,β-dichloro-n-butyric acid (low-melting isomer) (crotonic acid dichloride)* (3:1375).]

Colorless cryst. from pet. ether. — $\bar{C}$ is very eas. sol. alc., ether, much less sol. aq.

[For prepn. of $\bar{C}$ from α-chlorocrotonic acid (3:2760) by addn. of 1 HCl using conc. aq. HCl (satd. at 0°) in s.t. at 100° for 50 hrs. see (2) (4); from either α-chloro-β-hydroxy-n-butyric acid of m p. 62° [Beil. III-309] (4) or from β-chloro-α-hydroxy-n-butyric acid of m p. 125° [Beil. III-306] (3) by htg with conc. aq. HCl (satd. at 0°) in s.t at 100° for 40 hrs. see indic. refs.; for formn. of $\bar{C}$ by (partial) isomerization of the lower-melting isomer (crotonic acid dichloride) (3:1375) with conc HCl in s t. at 100° see (5); from the amide (see below) corresp. to $\bar{C}$ with HNO_2 see (1).]

$\bar{C}$ behaves as an acid but is slightly weaker than its isomer; ionization const. of $\bar{C}$ is $6\,1 \times 10^{-3}$ (5); its reported salts include $Ag\bar{A}$, spar sol. aq. (4), $Ba\bar{A}_2.3H_2O$ (4): and $Zn\bar{A}_2$ (4).

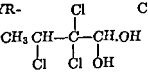
$\bar{C}$ with alc. KOH loses 1 mole HCl giving (2) (4) mainly α-chlorocrotonic acid (3:2760) accompanied by some α-chloro-isocrotonic acid (3:1615).

The acid chloride corresp. to $\bar{C}$ is unreported.

—— **Methyl α,β-dichloro-n-butyrate:** unreported.
—— **Ethyl α,α-dichloro-n-butyrate:** unreported.
—— **α,β-Dichloro-n-butyramide:** m.p. 125° (1). [Prepd. indirectly but with HNO_2 gives $\bar{C}$ (1).]

3:1903 (1) Rambaud, *Bull. soc. chim.* (5) **1**, 1339 (1934). (2) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 259–262 (1892). (3) Melikoff, Petrenko-Kritschenko, *Ann.* **266**, 371–374 (1891). (4) Melikoff, *Ann.* **234**, 201–204 (1886). (5) Michael, Bunge, *Ber.* **41**, 2911 (1908).

3:1905 **α,α,β-TRICHLORO-n-BUTYRALDEHYDE HYDRATE** ("Butyrchloral hydrate")



$C_4H_7O_2Cl_3$ Beil. I-664, I_1—, I_2-(725)

M.P. 78° (1)
77–78° (2)
77° (24)
74–74.5° (3)

[*See also α,α,β-trichloro-n-butyraldehyde (butyrchloral)* (3:5910).]

Lfts. from aq. or alc. — Spar. sol. cold but fairly eas. sol. hot aq.; very eas sol. alc. — For crystallographic data see (3) (5). — Note that because of tendency to dissociate on htg. into butyrchloral (3:5910) + aq. the m.p. observed for $\bar{C}$ varies according to rate of htg (3). — Note also that $\bar{C}$ is isomeric with chloral ethylalcoholate (3:0860) with which it must not be confused; for distinction of $\bar{C}$ from chloral hydrate (3:1270) see (9) (10).

$\bar{C}$ is employed in medicine as a sedative; from the body it is excreted in the urine as urobutyrochloralic acid [Beil. I-664], which upon hydrolysis yields (4) 2,2,3-trichlorobutanol-1 (3:1330) + glucuronic acid [Beil. III-884, III_1-(306)].

[For prepn. of $\bar{C}$ from butyrchloral (3:5910) by reactn. with aq. see (1) (2) (6).]

[$\bar{C}$ is reduced by fermenting yeast giving (7) dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°; for actn. of $\bar{C}$ on alc. fermentation see (8).]

$\bar{C}$ on oxidn. with 3 wt. pts. fumg. HNO_3 (D = 1.504) at 30–35° for 1½ hrs. then stood at room temp. for 24 hrs. gives (95% yield (11)) α,α,β-trichloro-n-butyric acid (3:1280).

$\bar{C}$ on distn. with half its wt. of Ac_2O (12), or shaking with conc. H_2SO_4 (13), or on distn. with $CHCl_3$ (14), *or on htg. alone loses its combined aq. yielding butyrchloral* (3:5910), b.p. 165°.

$\bar{C}$ with conc. H_2SO_4 (at least 6 wt. pts.) at room temp. for 2 days trimerizes to a mixt. (80% yield (12)) of two parabutyrchlorals: these are colorless crystn., sharp-melting solids, sol. in org. solvents, but insol. aq.; the less sol. α-parabutyrchloral, rhombic cryst. from boilg. AcOH or boilg. EtOH, has m.p. 180°; the more sol. β-parabutyrchloral (stereoisomer ?), cryst. from boilg. AcOH or boilg. EtOH, has m.p. 157°; these polymers can be distilled at 15 mm. but attempts to distil them at ord. press. result in complete dissociation to butyrchloral (3:5910).

$\bar{C}$ *with aq. KOH or NaOH evolves heat and yields* (1) (15) *1,1-dichloropropene-1* (3:5120) + the salt of formic acid (1:1005).

[$\bar{C}$ with conc. aq. HCN fails (16) to react, but upon addn. of alc. and subsequent digestion (16), or $\bar{C}$ (1 mole) with aq. KCN (2 moles) at 40° (17), gives (20% yield (17)) α,α,β-trichloro-n-butyraldehyde cyanohydrin [Beil. III-322, III_2-(226)], pl. from aq., m.p. 101–102° (17) (18), accompanied by (61% yield (17)) α-chlorocrotonic acid (3:2760), m.p. 98.5–99° (17). — Note that $\bar{C}$ (1 mole) in alc. treated gradually with powdered KCN (2 moles) below 15° over a 3–4 hr. period gives (90% yield (17)) ethyl α-chlorocrotonate (3:8523); in this reactn. the intermediate ethyl α,β-dichloro-n-butyrate readily loses HCl and is generally not isolated; use of alcs. other than EtOH gives good yields of the corresp. alkyl α-chlorocrotonates (17). — Note that for $\bar{C}$ with KCN in C_6H_6 the reaction takes a different course (17). — Finally, note that $\bar{C}$ (1 mole) in conc. aq. NH_4OH first dissolves, then ppts. butyrchloral-ammonia as a heavy oil; the mixt. on satn. with dry NH_3 gas in cold followed by treatment at 10° with powdered KCN (1 mole) evolves heat and gives (93% yield (17)) α-chlorocrotonamide, m.p. 113.5° (17).]

[$\bar{C}$ undergoes condensation with various org. systems: e.g., $\bar{C}$ with phenyl isocyanide (1 mole) in ether for 4–5 days gives (53% yield (19)) α-hydroxy-β,β,γ-trichloro-valeranilide, tbls. from alc., C_6H_6, or $CHCl_3$, m.p. 156–158° (19). — $\bar{C}$ (1 pt.) with malonic acid (1:0480) (1 pt.) in pyridine (1 pt.) at 100° for 3 hrs. evolves CO_2 and gives (20) β-hydroxy-γ,γ,δ-trichloro-n-caproic acid, cryst. from hot aq., m.p. 102° (20). — $\bar{C}$ (1 mole) with nitromethane (1½ moles) in dil. alc. in pres. of Na_2SO_3 at 60° gives (100% yield (21)) 1-nitro-3,3,4-trichloropentanol-2, b.p. 156° at 4 mm., m.p. abt. 20° (21); $\bar{C}$ (1 mole) with nitroethane (1 mole) in 50% alc. in pres. of Na_2SO_3 + K_2CO_3 at 70° gives (22) 2-nitro-4,4,5-trichlorohexanol-3, *b.p. 138° at 0.75 mm.* (22).]

[$\bar{C}$ forms with various org. substances molecular cpds. of pharmaceutical interest: e g., $\bar{C}$ (1 mole) with quinine (base) (1 mole) in abs. alc. at 75° for 1 hr. gives 1:1 cpd., m.p. 139° (note that the corresp. cpd. from chloral (3:5210) + quinine has m.p. 149° (23)). — $\bar{C}$ (1 mole) with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") (1 mole) (m.p. 112°) rubbed together and recrystd. from aq. gives (24) *1:1 molecular cpd, colorless pr., m.p. 72°* (for f.p /compn. data and diagram of this system see (24)). — $\bar{C}$ with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") (m.p. 107.5°) on fusion or in aq. or C_6H_6 (24) (25) (26) gives a 1:1 mol. cpd. ("Trigemin"), cryst. from C_6H_6, m.p. 85–86° (26), long ndls. from aq., m.p. 84° (24) (for f.p./compn. data and diagram on this system see (24)); for stabilization of "Trigemin" by addn. of 5–10% hexamethylenetetramine (27) or 2% MgO (28) see indic. refs.]

[$\bar{C}$ with various org. hydroxy acids in pres. of conc. H_2SO_4 condenses to give prods. of the chloralide type: e.g., for reactn. of $\bar{C}$ with citric acid (1:0505), malic acid (1:0450), or tartaric acid (1:0525) see (29); with gallic acid (1:0875) (and numerous other phenolic acids) see (30).]

$\bar{C}$ with conc. aq. NH_4OH first dissolves then ppts. a heavy oil of butyrchloral-ammonia (17); cryst. m.p. 62° (see also above for its reaction with KCN).

[$\bar{C}$ with excess dry NH_4OAc on moderate htg for several hrs, then pouring into aq., gives (18) α,α,β-trichloro-n-butyraldimine, cryst from C_6H_6, m p 169–170° (31), 164–165° (18); observe that this m.p. is notably close to that of the condensation prod. of butyrchloral (3:5910) with acetamide, and that latter is readily formed from NH_4OAc by dry htg.; *this matter, however, seems to have received no further attention.*]

$\bar{C}$ with aq. $NH_2OH.HCl$ on htg. readily yields (32) α,α,β-trichloro-n-butyraldoxime (first separating as an oil), cryst. from lgr, m p 65° (32)

The reaction of $\bar{C}$ with arylhydrazines is of special interest and has been extensively studied. With phenylhydrazine the reaction is extremely vigorous (33) (34) and unless carefully controlled (35) may become almost explosively violent yielding only tar. With nuclear-substituted phenylhydrazines, however, the reaction is milder, and their study has shown that all arylhydrazines react in the same general pattern although this comprises several different courses according to the solvent used The pattern will be illustrated here only by the case of 2,4-dichlorophenylhydrazine (see below); for details of the analogous reaction of $\bar{C}$ with phenylhydrazine (33) (34), o-, m-, and p-tolylhydrazines (34), 2,5-dichlorophenylhydrazine (35) (36), 3,5-dichlorophenylhydrazine (35), 2,4,5-trichlorophenylhydrazine (36), 2,4,6-trichlorophenylhydrazine (36), p-bromophenylhydrazine (34), 2,4-dibromophenylhydrazine (37), 4,5-dibromophenylhydrazine (35), and 2,4,6-tribromophenylhydrazine (35) see indic refs.

[The reactn. of $\bar{C}$ (1 mole) with 2,4-dichlorophenylhydrazine hydrochloride (1 mole) first gives the expected butyrchloral 2,4-dichlorophenylhydrazone (*A*) which, however, cannot be isolated because of immediate further reaction in two different modes according to the solvent employed. In dil aq. HCl contg NaOAc (*A*) loses HCl in two different ways leading on one hand to α,β-dichlorocrotonaldehyde 2,4-dichlorophenylhydrazone (*B*), long yel. pr. from alc. or AcOH, m.p. 112° (33), and on the other (simultaneously and with rearr. of unsatd. linkages) to the crimson 1-(2,4-dichlorobenzeneazo)-2,3-dichlorobutene-1 (*C*) (*in most instances the last is not isolatable in pure form although it has been in the case* (37) *of* $\bar{C}$ *with 2,4-dibromophenylhydrazine*), in MeOH, EtOH, or AcOH, however, the two α-chlorine atoms of the initial arylhydrazone (*A*) undergo hydrolysis with consequent formn. of β-chloro-α-keto-n-butyraldehyde 2,4-dichlorophenylhydrazone (*D*), pale yel. pr. from alc., m.p 129° (33).]

[This last type of cpd. (*D*) can be caused to undergo two further important types of reaction: e.g., (*D*) with further 2,4-dichlorophenylhydrazine in MeOH soln. not only undergoes conventional condensation of its α-keto grouping but also has the β-chlorine atom replaced by methoxyl so that the product obtd is β-methoxy-α-keto-n-butyraldehyde bis-(2,4-dichlorophenyl)osazone (*E*), bright yel pr from pyridine or C_6H_6, m.p. 196° dec. (33) (this reaction occurs so readily in MeOH that from $\bar{C}$ + 2,4-dichlorophenylhydrazine hydrochloride both (*D*) and (*E*) are formed and may be separated by fractional crystn.); on the other hand, (*D*) with alc. NaOEt on htg loses HCl and ring-closes (38) to 1-(2,4-dichlorophenyl)-4-hydroxy-5-methylpyrazole (*F*), colorless cryst. from boilg. alc., m.p. 184° (38) (this type of reactn. comprises a general synthesis of 4-hydroxypyrazoles).]

3:1905 (1) Krämer, Pinner, *Ber.* 3, 383 390 (1870) (2) Moureu, Murat, Tampier, *Bull. soc. chim.* (4) 29, 33 (1921). (3) Lieben, Zeisel, *Monatsh* 4, 534 538 (1883). (4) Mering, *Z. physiol. Chem.* 6, 471–496 (1882). (5) von Lang, *Z Krist.* 25, 521–522 (1896). (6) Pinner, *Ann.* 179,

26–29 (1875). (7) Rosenfeld, *Biochem. Z.* **156**, 54–57 (1925); *Cent.* **1925**, I 2301; *C.A.* **19**, 2683 (1925). (8) Neuberg, Ehrlich, *Biochem. Z.* **101**, 239–275 (1920); *Cent.* **1920**, I 534; *C.A.* **14**, 2007 (1920). (9) Gabutti, *Boll. chim. farm.* **42**, 777–778 (1903); *Cent.* **1904**, I 480. (10) Ware, *Chemist and Druggist* **123**, 282 (1935); *Cent.* **1936**, I 1667; *C.A.* **30**, 983 (1936).

(11) Roberts, *J. Chem. Soc.* **1938**, 770. (12) Chattaway, Kellett, *J. Chem. Soc.* **1928**, 2709–2714. (1 ... tessier, *Compt. rend.* **90**, ... Bischoff, *Ann.* **179**, 97–9 ... (18) Pinner, Klein, *Ber* ... (20) Riedel, Straube, *Ann.* **367**, 44 (1909).

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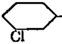
(31) Schiff, *Ber.* **11**, 2167 (1878). (32) Schiff, Tarugi, *Gazz. chim. ital.* **21**, II 8–9 (1891). (33) Chattaway, Irving, *J. Chem. Soc.* **1930**, 87–94. (34) Chattaway, Irving, *J. Chem. Soc.* **1931**, 751–753. (35) Chattaway, Irving, *J. Am. Chem. Soc.* **54**, 263–271 (1932). (36) Chattaway, Adair, *J. Chem. Soc.* **1933**, 1488–1490. (37) Irving, *J. Chem. Soc.* **1940**, 813–817. (38) Chattaway, Irving, *J. Chem. Soc.* **1931**, 786–791.

3:1910 3-CHLOROPHENYLACETIC ACID $C_8H_7O_2Cl$ Beil. S.N. 941
(*m*-Chloro-α-toluic acid)

 —$CH_2.COOH$

M.P. 77.5–78.5° cor. (1)
76° (2) (3)
74° (4)

Colorless ndls. best recrystd. from commercial *n*-heptane (Skellysolve "C") (1); lfts. from aq. alc. (4). — Very spar. sol. aq., quite sol. alc. or C_6H_6, misc. with ether. [For study of ionization const. see (3).] — [For study of fate of $\bar{C}$ in animals see (5).]

[For prepn. of $\bar{C}$ from *m*-chlorobenzyl bromide (m.p. 15–15.5° cor., b.p. 103–105° at 8 mm., $D_{25}^{25} = 1.5652$ (1)) via conversion to *m*-$Cl.C_6H_4.CH_2MgBr$ and subsequent carbonation (65–75% yield) see (1); from *m*-aminophenylacetic acid [Beil. XIV-456, XIV$_1$-(588)] *via diazotization and use of* Cu_2Cl_2 reactn. (but no details reported) (5); from *m*-chlorophenylpyruvic acid (4) in dil. aq. NaOH with 30% H_2O_2 (57% yield) see (4); from *m*-chlorophenylacetonitrile, m.p. 11.5°, b.p. 261° at 757 mm. (2), by hydrolysis in H_2SO_4/AcOH/aq. see (2).]

[For reactn. of closely related *m*-$Cl.C_6H_4.CH_2.COOMgX$ with large excess of various RMgX cpds. see (6) and also under *m*-chlorobenzyl chloride (3:6445).]

[$\bar{C}$ with $SOCl_2$ yields (5) *m*-chlorophenylacetyl chloride, yel.-green liq., b.p. 52° at 16 mm. (5); this prod. with aminoacetic acid *(glycine)* in dil. aq. NaOH *yields (5) m-chloro*phenylacetaminoacetic acid (*m*-chlorophenylaceturic acid), colorless ndls. from aq., m.p. 144–145° (5).]

[$\bar{C}$ converted to its Pb salt, latter dried at 110° and distilled, yields (2) 3,3′-dichlorodibenzyl ketone, colorless ndls. from alc. m.p. 89° (2) (corresp. oxime, m.p. 73° (2), semicarbazone, m.p. 121° (2)).]

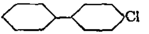
—— **Methyl 3-chlorophenylacetate:**
—— **Ethyl 3-chlorophenylacetate:**

(1) (3-Chlorophenylacet...

C̄ with 1 mole aniline on htg. at 180–190° for 2 hrs. (1), or indirectly from *m*-chlorobenzyl phenyl ketoxime by Beckmann rearr. with PCl_5 in ether (64–82% yield (1)).]

Ⓓ (3-Chlorophenylacet)-*m*-chloroanilide: white ndls. from dil. alc., m.p. 120° cor. (1). [From C̄ with *m*-chloroaniline (1 mole) on htg. at 180–190° for 2 hrs (1), or indirectly from *m*-chlorobenzyl *m*-chlorophenyl ketoxime by Beckmann rearr. with PCl_5 in ether (64–82% yield (1))]

3:1910 (1) Jenkins, *J. Am. Chem. Soc.* **55**, 2898–2899 (1933). (2) Kenner, Morton, *J. Chem. Soc.* **1934**, 679–680. (3) Dippy, Williams, *J. Chem. Soc.* **1934**, 1888–1892. (4) Buck, Ide, *J. Am. Chem. Soc.* **54**, 3307–3309 (1932). (5) Muenzen, Cerecedo, Sherwin, *J. Biol. Chem.* **68**, 503–510 (1926). (6) Ivanov, Pchnénitchny, *Bull. soc. chim.* (5) **1**, 231–232 (1934).

3:1912 4-CHLOROBIPHENYL  $C_{12}H_9Cl$ Beil. V - 579
(4-Chloro-xenene (15)) V_1—
V_2-(483)

M.P.	**77.7°**	(1)	B.P.	**291.2°**	at 745 mm. (5)
	77.5°	(2) (3)		**282°**	(12)
	77.2–77.4°	(4)		**222–226°**	at 150 mm. (14)
	77.2°	(5)			
	77°	(6) (7) (8)			
	76°	(9) (10) (21) (25)			
	75.5°	(11) (12)			
	75–76°	(13)			

Colorless cryst. from alc. (0.8 ml./g. (5)); somewhat less sol. in alc. than isomeric 2-chlorobiphenyl (3:0300). — Volatile with steam. — [For f.p./compn. curves of systems: C̄ + biphenyl (1:7175), C̄ + 4-fluorobiphenyl, or C̄ + 4-bromobiphenyl, see (7)]

[For prepn. of C̄ from biphenyl (1:7175) with Cl_2 in pres. of Fe (30% yield (5)) (14) (16) (17), or $SbCl_5$ (12), see indic. refs. (2-chlorobiphenyl (3:0300) is also formed; for use of mixt. for transformer oil see (18); for sepn. of mixt. see (19)); for prepn. of C̄ from *p*-aminobiphenyl via diazotization and use of Cu_2Cl_2 reactn. see (2) (7).]

[For prepn. of C̄ from *p*-chloroaniline [Beil. XII-607, XII_1-(604)] via diazotization and coupling of resultant diazonium salt with C_6H_6 in aq. NaOH suspension (yields: 41% (1), 40% (6)) cf. (21) (23) or in aq. NaOAc (yield = 35% (6)), or by formn. of *p*-chlorobenzenediazonium chloride/$ZnCl_2$ cpd. and reactn. of latter with C_6H_6 in AcOH + NaOAc (yield = 34% (20)) see indic. refs.: from *N*-nitroso-acet-*p*-chloroanilide with C_6H_6 in $CHCl_3$ for a few days at room temp. see (13).]

[For formn. of C̄ from decompn. of dibenzoyl peroxide (1:4930) in boilg. chlorobenzene see (22); from decompn. of benzoyl *p*-chlorobenzoyl peroxide see (23); from di-(*p*-chlorobenzoyl) peroxide in C_6H_6 see (24) (4) (3); for formn. of C̄ from 4-hydroxybiphenyl (1:1585) with PCl_5 see (10); from *p*-xenylselenium trichloride on htg. see (25); from *p*-chloroiodobenzene + Cu powder see (2)]

[C̄ with aq 15–30% NaOH at 300–400° under pressure (26) in pres. of Cu (27), or C̄ with aq. Na_2CO_3 + Cu at 300° (28), or C̄ with aq. vapor over cat. at 525–600° (29) gives (75% yield (26)) 4-hydroxybiphenyl (1:1585) (28) (29) or its mixt. with 3-hydroxybiphenyl (1:1475) (27).]

[C̄ with conc. aq. NH_4OH + cat. under press. as directed (30) (31) gives *p*-aminobiphenyl]

[C̄ with Li in dry ether under N_2 gives (32) Li *p*-xenyl. — C̄ with Na sand in C_6H_6 at 110–120° under press. followed by carbonation with CO_2 gives (65–67% yield (33)) biphenyl-4-carboxylic acid (*p*-phenylbenzoic acid) [Beil. IX-671, IX_1-(280)]. — C̄ with Na

+ diethyl carbonate (1:3150) in C_6H_6 as directed gives (yields: 42% (35), 35–40% (36), 39% (37), 23% (38)) tri-(*p*-xenyl)carbinol (*tris*-*p*-biphenylcarbinol) [Beil. VI-738, V_1-(369)], colorless cryst. from AcOH, m.p. 207–208° (36), 207° (38), 206–207° (37). — $\bar{C}$ with Na + benzophenone (1:5150) in C_6H_6 gives (67% yield (34)) diphenyl-*p*-xenylcarbinol [Beil. VI-732], colorless cryst. from lgr., stable form, m.p. 135–136° (34), metastable form, m.p. 112–113° (34).]

[For reactn. of $\bar{C}$ with Na + $AsCl_3$ giving (39) tri-(*p*-xenyl)arsine, with Na + $SbCl_3$ giving (40) tri-(*p*-xenyl)stibine, with Na + PCl_3 giving (41) tri-(*p*-xenyl)phosphine, or with Na + $SiCl_4$ giving (42) tetra-(*p*-xenyl)silane see indic. refs.]

[$\bar{C}$ + stearoyl chloride (3:9960) + $AlCl_3$ in CS_2 gives (43) heptadecyl *p*-chloroxenyl ketone, m.p. 96–97° (43). — $\bar{C}$ + cyclohexene (1:8070) + $AlCl_3$ gives (44) a mixt. of cyclohexyl-*p*-chlorobiphenyls.]

[$\bar{C}$ + phthalic anhydride (1:0725) + $AlCl_3$ as directed (45) (46) gives (93% yield (45)) *o*-[4-(*p*-chlorophenyl)benzoyl]benzoic acid, colorless rods from AcOH or toluene, m.p. 251° cor. (45), 249.6–250.6° (46).]

The nitration of $\bar{C}$ does not appear to have been reported.

$\bar{C}$ on oxidn. with CrO_3 in AcOH yields (10) (25) *p*-chlorobenzoic acid (3:4940), m.p. 237° (10) (25).

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(21) Bamberger, *Ber.* **29**, 465–466 (189[illegible] Rasuwajeu, *Ann.* **480**, 168–169 (1930). [illegible]

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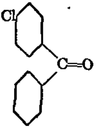
[illegible] humb, Ackerman, Saffer, [illegible] *Eng. Chem.* **29**, 194–196 [illegible] Aug. 14, 1934; *Cent.* **1935**, [illegible] ns, U.S. 1,786,526, 1,786,-



3:1914 4-CHLOROBENZOPHENONE (p-Chlorophenyl phenyl ketone) $C_{13}H_9OCl$ Beil. VII - 419 VII_1-(227)

M.P. 78.4°	(1)	B.P. 332° at 771 mm.	(7)
78°	(28)	322–325°	(8)
77–78°	(2)		
76–77°	(35)		
76°	(3) (4)		
75.5–76°	(5) (37)		
75–77°	(6)		
75°	(7)		
72–73°	(8)		

Colorless ndls. from alc., 80% alc., or ether + alc. — Eas. sol. hot alc. but spar. sol. cold alc., eas. sol. ether, spar. sol. cold lgr. [For search for possible polymorphic forms see (4) (9) (10).]

[For prepn. of C̄ from benzoic acid (1:0715) + chlorobenzene (3.7903) with $AlCl_3$ (82.4% yield C̄ + 11.9% 2-chlorobenzophenone (3:0715) (1)), or with P_2O_5 at 180–200° (5), see indic. refs.; from benzoyl chloride (3:6240) + chlorobenzene (3:7903) with $AlCl_3$ (yields: 97% (37), 86% (8), 80–90% (7) (11), 45% (4), 40% (2)) (3) (some 2-chloro isomer also being formed (12)) see indic. refs ; from p-chlorobenzoyl chloride (3:6550) + benzene with $AlCl_3$ (84.6% yield) see (6); from tetra-(4-chlorophenyl)ethylene glycol *bis*-(magnesium iodide) in quant. yield with I_2 or O_2 see (13); from p-chlorobenzohydrylidene-α-phenylethylamine by hydrol. with warm dil. H_2SO_4 see (8).]

[C̄ on reduction with Al/Hg in 80% alc. (3) (14) or with 3% Na/Hg (7) or on boilg. with alc. KOH for 2 days (15), or exposure to sunlight for 7 days of its soln. in isopropyl alc. contg. Na isopropylate, gives (85% yield (3) (14), 80% yield (16)) 4-chlorophenyl-phenylcarbinol (4-chlorobenzohydrol) [Beil. VI-680, VI_1-(327)], m.p. 67.5° (3) (14), 62° (7), accompanied by a little (14% (3) (14)) α,α'-diphenyl-α,α'-*bis*-(4-chlorophenyl)ethylene glycol (*sym.*-4,4'-dichlorobenzopinacol) [Beil. VI_1-(523)], m.p 179° (3) (14). — C̄ with Zn + AcOH yields 4-chlorobenzohydryl acetate (12) or a mixt. (7) of 4-chlorobenzohydrol (above) + the corresp. pinacol (see below).]

[C̄ with Mg + MgI_2 in ether + C_6H_6 or C̄ in very dil. alc. soln. in sunlight (7) gives (94% yield (13)) *sym.*-4,4'-dichlorobenzopinacol, m.p 172–178° (see above). — C̄ with Zn dust + H_2SO_4 in aq. AcOH yields (12) *sym.*-4,4'-dichloro-α-benzopinacoline (*sym.*-4,4'-dichlorotetraphenylethylene oxide) [Beil. $XVII_1$-(45)], ndls. from AcOH, m p. 220° dec. (12). — For oxidn.-reductn. potential of C̄ see (35)]

[C̄ with conc. HI + red P in AcOH refluxed 14 hrs. gives (7) 4-chlorodiphenylmethane [Beil. V-590, V_1-(278), V_2-(500)], b p. 298° at 742.5 mm. (7).]

[C̄ with diphenylmethyl sodium (benzohydryl-sodium) followed by aq. gives (18) corresp. tertiary alc., viz., benzohydryl-p-chlorophenyl-phenyl-carbinol, m.p. 176–178° (18), which with acetyl chloride loses H_2O to give 4-chlorotetraphenylethylene [Beil. V_1-(376), V_2-(679)], m.p. 166–167° (18). — C̄ with MeMgI in dry ether yields (19) p-chlorophenyl-phenyl-methyl-carbinol which on loss of aq. by htg. as directed gives (66% overall yield) α-(4-chlorophenyl)-α-phenylethylene, b.p. 164° at 16 mm. (19); note that this prod. with

Br_2 does *not* add halogen but rather evolves HBr yielding (20) both solid (m.p. 94–95°) and liq. stereoisomers of β-(4-chlorophenyl)-β-phenylvinyl bromide. — $\bar{C}$ with β-(4-chlorophenyl)-β-phenylvinyl MgBr as directed (23) gives 1,4-di-(p-chlorophenyl)-1,4-diphenylbutadiene-1,3, yellowish green ndls. from amyl alc., m.p. 230° (23). — $\bar{C}$ with triphenylmethyl MgBr in ether + C_6H_6, followed by dil. AcOH, gives (21) 78% yield *sym.*-4,4-dichlorobenzopinacol (see above) + 80% yield triphenylmethyl peroxide.]

[$\bar{C}$ with ethyl bromoacetate + Zn in dry C_6H_6 gives (yields: 79% (22), 67% (24)) ethyl β-(4-chlorophenyl)-β-hydroxy-β-phenyl-propionate, m.p 79–80.5° (22), 69° (24); this prod. on htg. with 85% formic acid gives (66% yield (24)) ethyl β-(4-chlorophenyl)cinnamate, b.p. 210–212° at 13 mm. (24), or on hydrolysis gives (22) β-(4-chlorophenyl)-β-hydroxy-β-phenylpropionic acid, m.p. 188.5–189.° dec. (22).]

$\bar{C}$ with PCl_5 at 150° gives (yields: 90% (25) (27), 88% (26) (8)) α,α,4-trichlorodiphenylmethane (4-chlorobenzophenone dichloride) [Beil. V-592, V_1-(279)], b.p. 191–193° at 13 mm. (8), 189–194° at 12 mm. (25). $D_4^{20} = 1.302$ (25), $n_D^{20} = 1.6110$ (25); this prod. with Zn dust refluxed in dry ether for 1 hr. gives (12% yield (25)) α,β-di-(p-chlorophenyl)-α,β-di(phenyl)ethylene, ndls. from alc., m.p. 202–203° (25).

$\bar{C}$ fused with KOH/NaOH gives (28) benzoic acid (66%) + p-chlorobenzoic acid (3:4940) (18%) + a little p-hydroxybenzoic acid (1:0840). — $\bar{C}$ with 10% aq. NaOH in pres. of Cu under press. at 190° yields (29) 4-hydroxybenzophenone (1:1560).

[$\bar{C}$ with NH_3 in pres. of Cu cpds. at 170–300° under press. gives (30) 4-aminobenzophenone [Beil. XIV-81, XIV_1-(388)], lfts. from dil. alc., m.p. 123–124°. — $\bar{C}$ condensed with $NaNH.C_6H_5$ as directed (31) yields 4-anilinobenzophenoneanil, m.p. 56° (for other amines and use of products as antioxidants see (31)); note, however, that by a closely similar method (36) p-chlorobenzophenoneanil, m.p. 64–64.5°, can also be obtd.]

$\bar{C}$ on dinitration with abs. HNO_3 gives (32) a mixt. contg. 4-chloro-3,3′-dinitrobenzophenone, cryst. from toluene, m.p. 166°, 4-chloro-3,2′-dinitrobenzophenone, cryst. from alc, m.p. 123.5°, and 4-chloro-3,4′-dinitrobenzophenone, m.p. 136–136.5°.

Ⓓ **4-Chlorobenzophenone oxime:** This prod. is known in two stereoisomeric forms: the higher-melting isomer, m.p. 155–156° (6) (corresp. acetate, m p. 147–148° (6), corresp. benzyl ether, m.p. 74–75° (6)), which on Beckmann rearr. (6) (34) with PCl_5, with conc. H_2SO_4 at 100°, or with $AcOH/Ac_2O/HCl$ yields 4-chlorobenzanilide, is in the light of modern views on *trans* interchange regarded as the *syn*-(p-chlorophenyl) stereomer; the lower-melting isomer, m.p. 95° (6) (corresp. acetate, m.p. 105–106° (6), corresp. benzyl ether, m.p. 98–99° (6)), which on Beckmann rearr. with PCl_5 yields benz-p-chloroanilide, is now regarded as the *trans*-(p-chlorophenyl) stereomer. [A mixt. of these two stereoisomeric oximes contg. 56% high-melting form + 44% low-melting form (33) is obtd. from $\bar{C}$ with $NH_2OH.HCl$ + pyridine in abs. alc. (33) or from $\bar{C}$ + $NH_2OH.HCl$ + dil. alc. KOH (6); the two isomers are separated by means of their different solubilities in alc. (6) (34). — Note that the lower-melting isomer is itself converted to the higher-melting form by htg. 3 hrs. at 100° (6) and also (in part) during Beckmann rearr.]

Ⓓ **4-Chlorobenzophenone phenylhydrazone:** cryst. from ether/AcOH, m.p. 106° (34). [From $\bar{C}$ with phenylhydrazine or phenylhydrazine acetate in alc. as directed (34).]

—— **4-Chlorobenzophenone p-nitrophenylhydrazone:** unreported.

Ⓓ **4-Chlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 184–185° (Heilbron).

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chim. **29**, 138, [illegible] (1927). (14) [illegible] 34–335 (1908).
(16) Bachmann, *J. Am. Chem. Soc.* **55**, 394 (1933). (17) Cohen, *Rec. trav. chim.* **39**, 258 (1920). (18) Bergmann, *J. Chem. Soc.* **1936**, 412–413. (19) Bergmann, Bondi, *Ber.* **64**, 1468 (1931). (20) Bergmann, Engel, Meyer, *Ber.* **65**, 456 (1932).

(21) Bachmann, *J. Am. Chem. Soc.* **53**, 2762 (1931). (22) Alexander, Jacoby, Fuson, *J. Am. Chem. Soc.* **57**, 2209 (1935). (23) Ref. 24, p. 256. (24) Bergmann, Hoffmann, Meyer, *J prakt. Chem.* (2) **135**, 261 (1932). (25) Price, Fanta, *J. Am. Chem. Soc. Soc.* **64**, 2726–2727 (1942). (26) Peterson, *Am. Chem. J.* **46**, 332 (1911). (27) Morgan, *J. Am. Chem. Soc.* **38**, 2100 (1916). (28) Lock, Rödiger, *Ber.* **72**, 868 (1939). (29) Britton (to Dow Chem. Co.), U.S. 1,961,630, June 5, 1934; *Cent.* **1934**, II 1846. (30) Britton (to Dow Chem Co.), U.S. 1,946,058, Feb. 6, 1934; *Cent* **1934**, I 3396

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3:1915 DI-(TRICHLOROMETHYL) CARBONATE

(Triphosgene, perchlorodimethyl carbonate, hexachlorodimethyl carbonate)

$(Cl_3CO)_2C{=}O$ $C_3O_3Cl_6$

Beil. III - **17**
III₁-(8)
III₂-(16)

M.P.		B.P.	
78–79°	(1)	203° at 760 mm., sl. dec.	(3)
79°	(2) (3) (4)	124° at 50 mm.	(3)
		117° at 36 mm.	(2)
		105° at 22 mm.	(2)

Cryst. from anhydrous ether (1) (2) or pet. eth. (4). — Disagreeable penetrating odor; attacks mucous membrane.

C̄ on distn. dissociates slightly into phosgene (3:5000) and diphosgene (trichloromethyl chloroformate) (3:5515) (4) (5); solid C̄ when mixed with powdered charcoal and heated to just above m.p. rapidly decomposes to phosgene (3:5000) (5).

[For prepn. of C̄ from dimethyl carbonate (1:3046) by chlorination in sunlight see (1); from methyl chloroformate (3:5075) by chlorination see (2).]

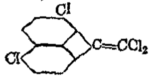
C̄ on treatment at 20° for 1 hr. with NaI in acetone evolves CO and separates iodine to 84% of amt. expressed by the reactn. $Cl_3C.O.CO.O.CCl_3 + 6NaI \rightarrow 3CO + 3I_2 + 6NaCl$ (6).

C̄ with most reagents behaves like phosgene; e.g., C̄ with alcohols gives ultimately dialkyl carbonates (7); C̄ with aniline in ether (7) or aq. (2) gives *N,N*-diphenylurea, m.p. 233° (7); C̄ with phenol + aq. NaOH gives (90% yield (7)) diphenyl carbonate (1:2335) cryst. from alc., m.p. 77.5–78° (7).

[For use of C̄ in prepn. of acid chlorides of carboxylic or sulfonic acids see (8); similarly C̄ htd. with anhydrous NaOAc yields Ac_2O (9).]

3:1915 (1) Councler, *Ber.* **13**, 1697–1699 (1880). (2) Grignard, Rivat, Urbain, *Ann. chim.* (9) **13**, 263–265 (1920). (3) Kling, Florentin, Jacob, *Ann. chim.* (9) **14**, 208–210 (1920). (4) Marotta, *Gazz. chim. ital.* **59**, 959 (1929) (5) Hood, Murdock, *J. Phys. Chem.* **23**, 508–512 (1919). (6) Perret, [illegible] (7) Nekrassow, Melnikov, *J. pr* [illegible] 4, 1033; *Cent.* **1934**, II 2133. (9) [illegible] 931); *C.A.* **26**, 3234 (1932); *Cent.* **1932**, II 2313.

3:1925 1,1-DICHLORO-2-(*o*-CHLOROPHENYL)-2-(*p*-CHLOROPHENYL) ETHYLENE $C_{14}H_8Cl_4$ Beil. S.N. 480



M.P. 78.4–79.5° cor. (1)

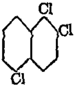
Rectangular pl. from MeOH or EtOH.

[For prepn. of C̄ from 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane ("*o,p'*-DDT") (3:1820) by elimination of 1 HCl with alc. KOH on refluxing 3 hrs. (97% yield) see (1).]

C̄ on oxidn. with CrO_3/AcOH gives (1) 2,4-dichlorobenzophenone (3:1565), m.p. 64.2–65.2° cor.

3:1925 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1599, 1602 (1945).

3:1930 1,2,5-TRICHLORONAPHTHALENE $C_{10}H_5Cl_3$ Beil. V-544 V_1— V_2—



M.P. 79° (1)
78–78.5° (2) (4)
77° (3)
(*See text.*)

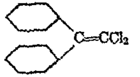
Cryst. volatile with steam. — C̄ if fused at 79° in cap. m.p. tube, and then allowed to cool slowly in the bath or rapidly in air, solidifies at 69° to a translucent cryst. mass which (if the temperature is immediately raised) melts at 74° but if allowed to remain at or below 69° for a few minutes becomes opaque and then melts at 79° (1).

[For prepn. of C̄ from 1-chloro-5-sulfonaphthylamine-2 [Beil. XIV-750] via diazotization and use of Cu_2Cl_2 reactn. see (1) (4); from 1-chloro-2-nitronaphthalenesulfonic acid-5 [Beil. XI-170] (3), 2-chloro-1-nitronaphthalenesulfonyl chloride-5 [Beil. XI-169] (3), 2-chloronaphthalene-1,5-*bis*-(sulfonyl chloride) [Beil. XI-213] (5), or 1,2-dichloronaphthalenesulfonic acid-5 [Beil. XI-163] (2) with PCl_5 see indic. refs.]

[C̄ treated with $ClSO_3H$ in CS_2 and conv. to K salt as directed (1) gives a mixt. contg. 70% (less sol.) K 1,2,5-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 146°) and 30% (more sol.) K 1,2,5-trichloronaphthalenesulfonate-Y (corresp. sulfonyl chloride, m.p. 179°).]

3:1930 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 251–252. (2) Armstrong, Wynne, *Chem. News* **59**, 188 (1889). (3) Cleve, *Chem. Ztg.* **17**, 398 (1893). (4) Armstrong, Wynne, *Proc. Chem. Soc.* **1889**, 36, 49. (5) Armstrong, Wynne, *Chem. News* **62**, 164 (1890).

3:1938 1,1-DICHLORO-2,2-DIPHENYLETHYLENE



$C_{14}H_{10}Cl_2$ Beil. V - 639, V_1—, V_2-(545)

M.P. 80°	(1) (2) (5) (6) (13)	B.P. 336° cor.	(5) (6)
78.0–79.5°	(3)	316.5° cor.	(7)
78.5°	(4)	315° u.c.	(5) (6)

Colorless cryst. from alc.; 100 pts. 90% alc. dis. in cold 11.91 pts. $\bar{C}$, on boilg. 19.87 pts. $\bar{C}$ *(8)*. — $\bar{C}$ is eas. sol. ether, $CHCl_3$, or CS_2; less so in alc. or C_6H_6.

PREPARATION OF $\bar{C}$

[For prepn. of $\bar{C}$ from *1,1,1-trichloro-2,2-diphenylethane (3:1420)* by splitting out 1 HCl on distn. (9) cf. (10) (6), or with alc. KOH (2) (1) (for study of rate see (11)), or alc. NaOEt (1) see indic. refs.; from *unsym.*-diphenylethane [Beil. V-605, V_1-(285), V_2-(509)] with Cl_2 at 100–150° in quartz flask in light for 10 hrs followed by distn. at ord. press. (16% yield) see (3); from *unsym.*-diphenylethylene [Beil. V-639, V_1-(308), V_2-(543)] with Cl_2 followed by distn. see (12).]

[For formn. of $\bar{C}$ from *α,α-dichloro-β,β-diphenylethylene sulfide* (Cl_2C—$C(C_6H_5)_2$ bridged by S) by htg. at 100° for 2 hrs. (or for shorter time at 160°), or by boilg. with MeOH, or htg. with Zn see (13); from *α,α-dichloro-β,β-diphenylethyl p-tolyl sulfone* with PCl_5 at 200° for 2 hrs. see (4); for formn. of $\bar{C}$ during condensation of chloral (3:5210) with C_6H_6 + $AlCl_3$ in CS_2 see (10) (6).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction. [$\bar{C}$ on reduction with conc. HI + P at 170–210° gives (7) *unsym.*-diphenylethane [Beil. V-605, V_1-(285), V_2-(509)] and bibenzyl (1:7149).]

Addition of halogens. $\bar{C}$ with Cl_2 in dry $CHCl_3$ adds 1 mole halogen giving (6) (5) 1,1,1,2-tetrachloro-2,2-diphenylethane, m.p. 85° (6). — $\bar{C}$ with excess Br_2 htd. on aq. bath until excess reagt. evaporates gives (6) 1,2-dibromo-1,1-dichloro-2,2-diphenylethane, cryst. from alc., m.p. 120.0–120.5° (6).

Behavior with alkalies. [$\bar{C}$ with aq. NaOH at 150°, or with alc. NaOH in s.t. at 100°, is substantially unaffected within 24 hrs. (3); however, $\bar{C}$ with alc. KOH in stainless-steel bomb at 150° for 24 hrs. gives (73% yield (3)) diphenylacetic acid (1:0765), m.p. 147–148° cor. (3) cf. (1). — Note also that, although $\bar{C}$ with dry NaOMe in C_6H_6 does not react even in s.t. at 180° for 36 hrs. yet $\bar{C}$ with dry NaOMe (2 moles) on direct distn. gives diphenylacetylene (tolane) and other products (15).]

[Note also that $\bar{C}$ with Na phenolate at 225° for 24 hrs. gives (3) α-hydroxy-α,α-diphenylacetaldehyde diphenylacetal (benzilaldehyde diphenylacetal), m.p. 111.5°–112° (3).]

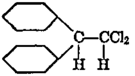
Behavior with H_2SO_4 or HNO_3. *With H_2SO_4.* $\bar{C}$ with conc. H_2SO_4 on warming first becomes yellow, then dark green, later violet, and ultimately brownish red. (5) (6).

With HNO_3. $\bar{C}$ on addition to 12 pts. ice-cold fumg. HNO_3 and subsequently pouring onto ice gives (14) 1,1-dichloro-2,2-*bis*-(*p*-nitrophenyl)ethylene, yellowish ndls. from hot alc., m.p. 172° (14); note also that from the mother liquors of recrystn. there can also be obtd. some 4,4′-dinitrobenzophenone, m.p. 188–189°, resulting from some simultaneous oxidn. (14).

Behavior with active metals. [C̄ with Li in dry ether followed by treatment with alc. gives according to conditions (16) (17) (18) either or both 1,2,3-triphenylnaphthalene, m.p. 151–152° (16) (17) (18) (mononitro deriv., m.p. 200–201° (18)), and 1,2,3,4-tetraphenylbutadiene-1,3, m.p. 183° (18) (17) (16); for explanation see (18).]

3:1938 (1) Harris, Frankfurter, *J. Am. Chem. Soc.* **48**, 3147–3148 (1926). (2) Bayer, *Ber.* **6**, 223 (1873). (3) Sheibley, Prutton, *J. Am. Chem. Soc.* **62**, 840–841 (1940). (4) Kohler, Potter, *J. Am. Chem. Soc.* **57**, 1321 (1935). (5) Biltz, *Ann.* **296**, 240–241 (1897). (6) Biltz, *Ber.* **26**, 1955–1956 (1893). (7) Redsko, *J. Russ. Phys.-Chem. Soc.* **21**, 424 (1889). (8) Elbs, *J. prakt. Chem.* (2) **47**, 78 (1893). (9) Goldschmiedt, *Ber.* **6**, 987 (1873). (10) Biltz, *Ann.* **296**, 221 (1897). (11) Brand, Busse-Sundermann, *Ber.* **75**, 1822, 1828 (1942). (12) Hepp, *Ber.* **7**, 1411 (1874). (13) Staudinger, Siegwart, *Helv. Chim. Acta* **3**, 846 (1920). (14) Lange, Zufall, *Ann.* **272**, 2–3 (1892). (15) Staudinger, Rathsam, *Helv. Chim. Acta* **5**, 648, 654 (1922). (16) Schlenk, Bergmann, *Ann.* **463**, 72–75, 80–81 (1928). (17) Bergmann, Schreiber, *Ann.* **500**, 118–120 (1933). (18) Smith, Hoehn, *J. Am. Chem. Soc.* **63**, 1184–1187 (1941).

3:1940 1,1-DICHLORO-2,2-DIPHENYLETHANE $C_{14}H_{12}Cl_2$ Beil. V - 606; V_1-(285); V_2-(510)



M.P. 80° (1) (2) **B.P. 295–305° dec.** (1)
74–75° cor. (3)
74° (4) (6)

Colorless cryst. from alc. — C̄ is eas. sol. alc., ether, acetone, AcOH, lgr., or $CHCl_3$. — C̄ with conc H_2SO_4 or with $AlCl_3$ gives a red color.

[For prepn. of C̄ from dichloroacetaldehyde diethylacetal (3:6110) with C_6H_6 + conc. H_2SO_4 (1) (5) (3) (yields not reported) see indic. refs.; for formn. of C̄ from dichloroacetaldehyde (3:5180) with C_6H_6 + $AlCl_3$ (6), or from 1,1,1-trichloro-2,2-diphenylethane (3:1420) during reduction in alc./pyridine with H_2 + Ni (7) or during electrolytic reduction as specified (8) (9) (2), see indic. refs.]

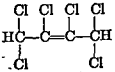
C̄ on distn. at ord. press. (1) or with boilg. alc. KOH (1) or NaOH (2) loses HCl giving 1-chloro-1,2-diphenylethylene [Beil. V-639], m.p. 42°. — Note, however, that C̄ with KNH_2 in liq. NH_3 (3) (5) not only loses HCl but the resulting intermediate reacts further with rearrangement giving (91% yield) diphenylacetylene (tolane) [Beil. V-656, V_1-(319), V_2-(568)].

C̄ on boilg. with aq. is *not* hydrolyzed and no trace of the expected diphenylacetaldehyde results (1).

C̄ on addition to fumg. HNO_3 at 0°, stdg. 24 hrs., and pouring into aq. gives (1) a dinitrobenzophenone of unknown structure (corresp. phenylhydrazone, m.p. 234° (1)).

3:1940 (1) Buttenberg, *Ann.* **279**, 324–327 (1894). (2) Brand, *Ber.* **46**, 2937–2941 (1913). (3) [illegible] (4) Combes, *Ann. chim.* (6) **12**, [illegible] 934). (6) Delacre, *Bul*[illegible] *n.* (2) **115**, 353, 361 (19[illegible] (1921).

3:1945 1,1,2,3,4,4-HEXACHLOROBUTENE-2 (solid stereoisomer) $C_4H_2Cl_6$ Beil. S.N. 11



M.P. 80° (1)

[*See also liquid stereoisomer* (3:9046).]

Colorless shining lfts. (from alc.) with camphoraceous odor. Eas. sol. ether, C_6H_6, $CHCl_3$, or CCl_4.

[For prepn. of C̄ (100% yield (1)) from the solid stereoisomer (3:0870) of 1,2,3,4-tetrachlorobutadiene-1,3 see (1); *for formn. of C̄ from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by actn. of u.v. light see (1).*] [*Note that octachlorobutane (3:2000)* has also been reported in same reactn.] [For formn of C̄ together with its liquid stereoisomer (3:9046) by actn. of Cl_2 upon the high-boilg. fraction obtd in the prepn. of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1).]

C̄ in alc. refluxed with Zn/Cu couple for 1 hr. yields (1) the solid stereoisomer of 1,2,3,4-tetrachlorobutadiene-1,3 (3:0870), m.p. 50° (1).

3:1945 (1) Müller, Hüther, *Ber.* **64**, 589–600 (1931); *C.A.* **25**, 3956–3957 (1931).

3:1960 PIPERONYLOYL CHLORIDE (3,4-Methylenedioxybenzoyl chloride) $C_8H_5O_3Cl$ **Beil. XIX - 270** XIX_1—

M.P. 80° (1) (2) **B.P. 155°** at 25 mm. (2) **140–141°** at 8 mm. (1)

[For prepn. of C̄ from piperonylic acid (1:0865) with excess $SOCl_2$ at 100° (1) or in C_6H_6 (90–95% yield (4)), or with PCl_5 (2), see indic. refs. — Note, however, that at higher temps. the dioxymethylene group is also attacked: e g, piperonylic acid htd. in a s.t. with $SOCl_2$ at 180–200° for 8 hrs. (1) or refluxed 3 hrs. with 3 moles PCl_5 (1) yields *μ,μ*-dichloropiperonoyl chloride (Beil. XIX-272, XIX_1-(743)], b p. 149–150° at 12 mm. (1).]

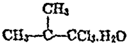
[C̄ with diazomethane yields (3) piperonyl diazomethyl ketone which with ammonia yields (3) homopiperonylamide, m.p. 173°; C̄ with ethyl sodio-acetoacetate in dry ether, followed by hydrolysis (as specified (4)) of the acetyl group, yields ethyl piperonoylacetate, m p. 42 5° (4).]

C̄ on hydrolysis with aq. yields piperonylic acid (1:0865), m p. 228°.

- ⓓ Piperonylamide [Beil. XIX-270]: tbls. from alc., m.p. 169°.
- ⓓ Piperonylanilide [*N*-phenyl-piperonylamide]: cryst. from dil. alc., m.p. 146–147° cor. (5). [From C̄ + 2 moles aniline in C_6H_6 (5).]
- ⓓ *Piperonylo-p-toluidide: cryst. from dil. alc., m.p. 149–149 5° cor. (5).* [Similarly using *p*-toluidine (5).]
- ⓓ Piperonylo-*α*-naphthalide: cryst. from dil. alc., m.p. 192–193° cor. (5). [Similarly using *α*-naphthylamine (5).]
- ⓓ Piperonylo-*β*-naphthalide: cryst. from dil. alc., m.p. 156 5–157° cor. (5). [Similarly using *β*-naphthylamine (5).]

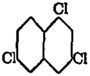
3:1960 (1) Barger, *J. Chem. Soc* **93**, 567–568 (1908). (2) Perkin, Robinson, *Chem. News* **92**, 293 (1905). (3) Arndt, Eistert, Ger. 650,706, Sept 30, 1937; *Cent.* **1937**, II 4390, *C.A.* **32**, 595 (1938). (4) Bruchhausen, Gerhard, *Ber.* **72**, 835–836 (1939). (5) Gertler, Haller, *J. Am. Chem. Soc.* **64**, 1741 (1942).

— **1,1,1-TRICHLORO-2-METHYL-PROPANOL-2 HYDRATE**



M.P. 80–81°

See 3:2062 *under anhydrous product.*

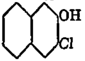
3:1975 1,3,6-TRICHLORO-NAPHTHALENE  $C_{10}H_5Cl_3$ Beil. V - 545
V_1—
V_2—

M.P. 80.5°–81° (1) (2)

[For prepn. of C̄ from 3,6-dichloronaphthalenesulfonyl chloride-1 (1), from 6-chloronaphthalene-1,3-*bis*-(sulfonyl chloride) [Beil. XI-212] (2), from 3-chloronaphthalene-1,6-*bis*-(sulfonyl chloride) [Beil. XI-214] (2), from 1-chloronaphthalene-3,6-*bis*-(sulfonyl chloride) [Beil. XI-217] (3), or from 1-nitronaphthalene-3,6-*bis*-(sulfonyl chloride) [Beil. XI-218] (1) (3) (4), each with PCl_5 as directed, see indic. refs.]

[C̄ treated with $ClSO_3H$ in CS_2 and prod. converted to sodium salt yields (1) sodium 1,3,6-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 156° (1)).]

3:1975 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 253, 256. (2) Armstrong, Wynne, *Chem. News* **62**, 164–165 (1890). (3) Armstrong, Wynne, *Chem. News* **71**, 254 (1895). (4) Armstrong, Wynne, *Proc. Chem. Soc.* **1895**, 81.

3:1990 1,3-DICHLORONAPHTHOL-2  $C_{10}H_6OCl_2$ Beil. VI - 649
VI_1—
VI_2-(604)

M.P. 80–81° (1)
78° (2)

Ndls. from lgr.; eas. sol. alc., ether, AcOH, or C_6H_6 (1).

[For prepn. see Beil. VI-649 and (2).]

C̄ in AcOH oxidized with conc. HNO_3 (D = 1.42) yields mainly 3-chloronaphthoquinone-1,2 [Beil. VII-720], red ndls. from $CHCl_3$, m.p. 172° (1).

C̄ in alc. boiled 15 hrs. with coppered Zn dust yields 3-chloronaphthol-2 (3:2545), m.p. 93° (4); but C̄ is not reduced by Na/Hg (3).

[For study of reaction of C̄ with alkali sulfites see (5).]

Ⓓ **1,3-Dichloro-2-naphthyl acetate:** from C̄ + AcCl; m.p. 79–80° (1). [Note that this m.p. is close to that of original C̄.]

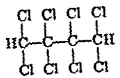
3:1990 (1) Zincke, *Ber.* **21**, 3385–3387 (1888). (2) Fries, Schimmelschmidt, *Ann.* **484**, 297 (1930). (3) Marschalk, *Bull. soc. chim.* (4) **43**, 1361 (1928). (4) Herzberg, Spengler, Schmid (to I.G.), Ger. 431,165, June 30, 1926; *Cent.* **1926**, 1196 (1926). (5) Marschalk, *Bull. soc. chim.* (4) **45**, 651–662 (1929).

CHAPTER VI

DIVISION A. SOLIDS

(3:2000-3:2100)

3:2000 1,1,2,2,3,3,4,4-OCTACHLOROBUTANE $C_4H_2Cl_8$ Beil. S.N. 10



M.P. 81° (1)

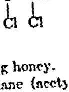
Colorless cryst. from alc. with odor resembling honey.

[For formn. of C̄ from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by protracted action of ultra-violet light see (1), considerable amts. of dichloroacetic acid (3:6208), m.p. 10.85°, and small amts. of oxalic acid (1:0445) are also formed (1), and the solid stereoisomer (3:1045) of 1,1,2,3,4,4-hexachlorobutene-2, m.p. 81° has also been reported (3) from the same reaction.]

[An octachlorobutane of m.p. 75.0–76.0° obtd. (2) from trichloroethylene (3:5170) by actn. of F_2 is not regarded (2) as having the structure of C̄.]

3:2000 (1) Müller, Luber, *Ber.* **65**, 985–987 (1932). (2) Miller, *J. Am. Chem. Soc.* **62**, 343 (1940). (3) Müller, Hüther, *Ber.* **64**, 599 (1931).

3:2100 2,4,5-TRICHLOROTOLUENE $C_7H_5Cl_3$ Beil. V - 290, V_1-(152), V_2-(232)



M.P. 82.4°	(1)	B.P. 229–230° at 716 mm. (2)	
82°	(2) (3) (4) (5)	230°	at 715 mm. (4)
81–82°	(8) (13)		
80–81°	(6)		

White ndls. or lfts. from alc. [For sepn. of C̄ from 2,3,4-trichlorotoluene (3:0125) by sulfonation of latter under conditions not affecting C̄ see (2) (7).]

[For prepn. of C̄ from 4,5-dichloro-2-aminotoluene [Beil. XII-837] (8), or from 4,6-dichloro-3-aminotoluene [Beil. XII-872] (8) (5), or from 2,5-dichloro-4-aminotoluene [Beil. XII-990] (3), via diazotization and use of Cu_2Cl_2 reactn. see indic. refs.; from toluene + $AlCl_3$ with SO_2Cl_2 at 70° (40% C̄ + 31% 2,3,4-trichlorotoluene (3:0125) (1)) see (1).]

[For formn. of C̄ (together with other products) from toluene with Cl_2 (9) in pres. of I_2 (10) or $MoCl_5$ (11) or $FeCl_3$ (11) on silica gel (4), or by electrolysis in HCl/AcOH soln. (12), see indic. refs.; from o-chlorotoluene (3:8245) or p-chlorotoluene (3:8257) with Cl_2 in pres. of $MoCl_5$ or $FeCl_3$ see (2); from 2,4-dichlorotoluene (3:6230) in pres. of Al/Hg

(13) or Fe (6) or from 3,4-dichlorotoluene (3:6355) in pres. of Al/Hg (13) see indic. refs.; from sodium *p*-toluenesulfonate with Cl_2 see (14).]

[$\bar{C}$ with Cl_2 yields (15) 2,4,5-trichlorobenzal dichloride (3:6910) (together with other products).]

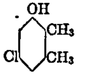
$\bar{C}$ on mononitration, e.g., by soln. in HNO_3 (D = 1.52) yields (16) (2) (8) 2,4,5-trichloro-3-nitrotoluene [Beil. V-333], ndls. from alc., m.p. 92° (2), 91–92° (8), 88.5–90.5° (17), 88.5° (16) (note that the isomeric 2,4,5-trichloro-6-nitrotoluene (prepd. indirectly (18)) has m.p. 93–94° (18)); $\bar{C}$ on dinitration, e.g., on warming with a mixt. of HNO_3 (D = 1.5) + conc. H_2SO_4, yields (16) (2) (8) 2,4,5-trichloro-3,6-dinitrotoluene [Beil. V-346], ndls. from alc., m.p. 227° (1) (2), 226–227° (8), 226° u.c. (18), 225° (16).

$\bar{C}$ on oxidn. with $K_2Cr_2O_7$ + H_2SO_4 (19) or with dil. HNO_3 in s.t. at 150° (8) (6) yields 2,4,5-trichlorobenzoic acid (3:4630) q.v.

3:2100 (1) Silberrad, *J. Chem. Soc.* **127**, 2681 (1925). (2) Seelig, *Ann.* **237**, 131, 140, 156 (1887). (3) Morgan, Drew, *J. Chem. Soc.* **117**, 789 (1920). (4) Firth, Smith, *J. Chem. Soc.* **1936**, 339. (5) Musante, Fusco, *Gazz. chim. ital.* **66**, 645 (1936). (6) Feldman, Kopeliowitsch, *Arch. Pharm.* **273**, 493–495 (1935). (7) Prentzell, *Ann.* **296**, 181–182 (1897). (8) Cohen, Dakin, *J. Chem. Soc.* **81**, 1332–1335 (1902). (9) Limpricht, *Ann.* **139**, 326 (1866). (10) Beilstein, Kuhlberg, *Ann.* **146**, 326 (1868).

(11) Aronheim, Dietrich, *Ber.* **8**, 1405 (1875). (12) Fichter, Glantzstein, *Ber.* **49**, 2481–2487 (1916). (13) Ref. 8, pp. 1340–1343. (14) British Dyestuffs Lds., Green, Clibben, Brit. 169,025, Oct. 13, 1921, *Cent.* **1922**, IV 376. (15) Leopold Cassella Co., Ger. 363,290, Nov. 6, 1922; *Cent.* **1923**, II 482–483. (16) Schultz, *Ann.* **187**, 277, 280 (1877). (17) Qvist, Holmberg, *Acta Acad. Aboensis Math. et Phys.* **6**, No. 14, 3–28 (1932); *Cent.* **1932**, II 2815–2816; *C.A.* **27**, 5726–5727 (1933). (18) Levy, Stephen, *J. Chem. Soc.* **1931**, 78. (19) Jannasch, *Ann.* **142**, 301 (1867).

3:2115 5-CHLORO-2,3-DIMETHYLPHENOL (5-Chloro-*o*-3-xylenol)



C_8H_9OCl Beil. VI — ; VI_1—; VI_2-(454)

M.P. 82° (1)
81–82° (2)

Ndls. from hot lt. pet. in which it is readily sol. hot but spar. sol. cold. — Volatile with steam.

[For prepn. of $\bar{C}$ from 5-amino-2,3-dimethylphenol (5-amino *o*-3-xylenol) [Beil. $XIII_1$-(244)] (3) via diazotization and use of Cu_2Cl_2 reaction (yield not stated) see (2); for formn. of $\bar{C}$ from 4,5-dichloro-1,1-dimethylcyclohexen-5-one-3 on htg. see (1).]

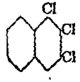
$\bar{C}$ with Cl_2 in lt. pet. gives (2) 4,5,6-trichloro-2,3-dimethylphenol (3:4742), m.p. 180–181°.

The nitration of $\bar{C}$ has not been reported, and none of the products to be expected is known.

—— **5-Chloro-2,3-dimethylphenyl acetate:** unreported.

Ⓓ **5-Chloro-2,3-dimethylphenyl benzoate:** pr. from alc., m p. 88° (2).

3:2115 (1) Hinkel, *J. Chem. Soc.* **125**, 1852 (1924). (2) Hinkel, Collins, Ayling, *J. Chem. Soc.* **123**, 2970–2971 (1923). (3) Crossley, *J. Chem. Soc.* **103**, 2181 (1913).

3:2125 1,2,3-TRICHLORONAPHTHALENE  $C_{10}H_5Cl_3$ Beil. V - 544
V_1—
V_2—

M.P. 82–83° (1)
81° (2)
80.5° (1)
(*See text.*)

Pr. from ether + alc. — The behavior of $\bar{C}$ on fusion is characteristic: if the fused $\bar{C}$ in a m.p. tube is allowed to cool to 68° and then withdrawn, it immediately solidifies to a translucent mass which on swift reimmersion into the bath shows m.p. 66–67° but if left for a few seconds in the air suddenly becomes opaque forming a cylinder of m.p. 82–83°, retracted from the wall of the capillary m.p. tube. This change (although slower) also occurs in the translucent form if cooled below 66° (1).

[For prepn. of $\bar{C}$ from 1-chloronaphthalene tetrachloride [Beil. V-493] with alc. NaOEt (61.6% yield (1)) (2) (3) see indic. refs.; from 1,3-dichloronaphthol-2 (3:1990) by distn. with PCl_5 see (2); from sodium 1,2,3-trichloronaphthalenesulfonate-7 (1) by hydrolysis with superhtd. steam see (1).]

[$\bar{C}$ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to sodium salt as directed (1) gives mixt. of sodium 1,2,3-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 131°, corresp. sulfonamide, m.p. 249°) and sodium 1,2,3-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 157°, corresp. sulfonamide, m p. 245°) (1).]

[$\bar{C}$ with 7 pts. fumg. H_2SO_4 (10% SO_3) shaken 15 min. at 100° yields (1) 1,2,3-trichloronaphthalene-5,7-disulfonic acid (corresp. *bis*-(sulfonyl chloride), m.p. 184° (1)).]

3:2125 (1) Turner, Wynne, *J. Chem Soc.* **1941**, 248–251. (2) Faust, Saame, *Ann.* **160**, 71 (1871). (3) Armstrong, Wynne, *Chem. News* **61**, 285 (1890).

3:2145 β,β-DICHLORO-α-HYDROXYISO-BUTYRIC ACID $C_4H_6O_3Cl_2$ Beil. III - 317
III_1—
III_2-(224)

$$Cl_2CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}COOH$$

M.P. 82–83° (1) (2) Neut. Eq. 173

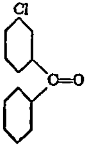
Pr. from EtOH/ether (1). — Cannot be distd. without decompn. but sublimes.

[For prepn. from β,β-dichloro-α-hydroxyisobutyronitrile (addn. prod. from α,α-dichloroacetone (3:5430) + HCN) [Beil. I-317] by digestion with strong HCl at 100° see (1).]

The corresp. anilide has been prepd. indirectly by interaction of phenyl isocyanide with α,α-dichloroacetone (3:5430) in aq. (2); pr. from $CHCl_3$, m p. 132–133° (2).

3:2145 (1) Bischoff, *Ber.* 8, 1334 (1875). (2) Passerini, *Gazz. chim. ital.* **54**, 540 (1924).

3:2160 3-CHLOROBENZOPHENONE (*m*-Chlorophenyl phenyl ketone) $C_{13}H_9OCl$ Beil. VII - 419 VII_1-(227)



M.P. 82–83° (1) (6)
82° (2) (3)
81° (4) (5)

Microscopic ndls. from alc. (1) (6) or *n*-PrOH (2); spar. sol. alc. (1), pet. ether (6), eas. sol. C_6H_6 (6).

[For prepn. from *m*-chlorobenzoyl chloride (3:6590) + C_6H_6 + $AlCl_3$ (64.7% yield (2)) see (2) (1) (6) (5).]

$\bar{C}$ on reduction with Na/Hg + alc. (100% yield (7)) or Al/Hg + 80% alc. (4) or boilg. alc. KOH (8) yields exclusively 3-chlorodiphenylcarbinol [Beil. VI_1-(327)], m.p. 40° (7), 39–40° (5), 38° (4). — $\bar{C}$ with Zn + AcOH (7) or $\bar{C}$ in alc. on long exposure to sunlight (7) gives *sym.*-3,3′-dichlorobenzpinacol [Beil. VI_1-(523)], cryst. from pet. eth., m.p. 137–138° (7), 135° (4).

$\bar{C}$ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (3) BzOH (1:0715) (80% yield (3)) and a little (5% (3)) *m*-chlorobenzoic acid (3:4392), m.p 158° (3), together with chlorobenzene (3:7903) from cleavage of most of the *m*-chlorobenzoic acid

$\bar{C}$ with CH_3MgI yields (2) 1-(*m*-chlorophenyl)-1-phenylethylene, oil, b.p. 152–153° at 14 mm. (2).

Ⓓ 3-Chlorobenzophenone oxime: from $\bar{C}$ + $NH_2OH.HCl$ + alk.; the two stereoisomers are sepd. by fractnl. pptn. of their AcOH soln. with aq. (1).

α-form (less-sol. isomer); cryst. pdr., m.p. 132–133° (1). [With PCl_5 in dry ether, followed by aq., this form yields *m*-chlorobenzanilide [Beil. XII-267], cryst. from alc., m.p. 122–125° (1).]

β-form (more-sol. isomer); cryst. pdr., m.p. 105–106° (1). [With PCl_5 in dry ether, followed by aq., this forms benz-*m*-chloroanilide [Beil. XII-605], ndls. from alc., m.p. 118° (1), *accompanied by some m-chlorobenzanilide (see above)* (1).]

3:2160 (1) Hantzsch, *Ber.* **24**, 57–58 (1891). (2) Bergmann, Bondi, *Ber.* **64**, 1477 (1931). (3) Lock, Rödiger, *Ber.* **72**, 867 (1939). (4) Cohen, Böeseken, *Rec. trav. chim.* **38**, 115, 123 (1919). (5) Norris, Blake, *J. Am. Chem. Soc.* **50**, 1812 (1928). (6) Koopal, *Rec. trav. chim.* **34**, 153 (1915). (7) Ref. 6, pp. 160–161. (8) Montagne, van Charante, *Rec. trav. chim.* **31**, 312 (1912)

3:2170 γ-CHLOROCROTONIC ACID (4-Chlorobuten-2-oic acid-1) $C_4H_5O_2Cl$ Beil. II - 418 II_1— II_2—

$$\underset{\displaystyle Cl}{CH_2}\!-\!CH\!=\!CH.COOH$$

M.P. 83° (1) B.P. 117–118° at 13 mm. (5)
82° (2)
81–82° (3) (4)

White cryst., eas. sol. ether or AcOH, can be recrystallized from pet. ether (1) or from hot aq. (5). — $\bar{C}$ distils under reduced press. without decomposition (5). — Note that m.p. 76.7–77.5° first reported (5) was later (2) found to be erroneous and same sample had actually m.p. 81–82° (2).

Note that, although C̄ is capable of existing in two geometrically isomeric forms, only this one is known; collateral evidence (but not actual proof) indicates that C̄ probably represents the *trans* stereoisomer.

[For prepn. of C̄ from ethyl γ-chlorocrotonate (3:8657) by hydrolysis with $Ba(OH)_2$ below 0° (60% yield (1) (6)) (4), or less advantageously with 30% aq. KOH in alc. soln. at −15° (40% yield (1)) (5) (note that γ-chlorovinylacetic acid, m.p. 10° (1), is often obtd. (1) (4) as by-prod.); for formn. of C̄ from β-γ-dichloro-*n*-butyric acid [Beil. II-280] with KOH (poor yield (5)), from *trans*-γ-hydroxycrotonic acid [Beil. III-376] with $SOCl_2$ in pyridine (2), or from methyl α-chloro-α-vinylacetate by hydrolysis (3) (7) (presumably as a result of allylic transposition of α-chloro-α-vinylacetic acid under the influence of alkali) see indic. refs.]

C̄ dissolved in excess aq. 1 *N* NaOH and shaken with H_2 in pres. of Pd/activated carbon is readily dehalogenated giving (95% yield (1)) crotonic acid (1:0425); with sufficient H_2 this prod ultimately reduces to *n*-butyric acid (1:1035).

[C̄ by cat. hydroxylation with $BaClO_3$/osmic acid gives (yields: 75% (6), 78% (9)) *threo*-γ-chloro-α,β-dihydroxy-*n*-butyric acid, m p 100° (9); this prod. with silver oxide as directed replaces Cl by OH giving (59% yield (6)) *d,l*-threonic acid, m.p 98° (6).]

C̄ adds Br_2 (1 mole) yielding (3) γ-chloro-α,β-dibromo-*n*-butyric acid, cryst. from cyclohexane, m.p. 119–120° (3)

C̄ with NaI in dry acetone ppts. NaCl and gives (86% yield (1)) γ-iodocrotonic acid, yel ndls. from lgr., m.p. 108–108.5° (1).

[C̄ on neutralization with NH_4OH and htg. with $(NH_4)_2SO_3$ at 50° for 12 hrs. gives (4) γ-sulfocrotonic acid, very hygroscopic cryst., m.p. 94–96°.]

The acid chloride corresponding to C̄ is unreported.

—— Methyl γ-chlorocrotonate: unreported.

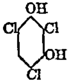
—— Ethyl γ-chlorocrotonate: b.p. 191–193° at 760 mm. (5) (see 3:8657).

—— γ-Chlorocrotonamide: cryst. from hot aq., m.p. 135.5–136° (8), 130–132° (5). [Reported only by partial hydrolysis of γ-chlorocrotononitrile (5) (8).]

—— γ-Chlorocrotonanilide: unreported.

3:2170 (1) Braun, *J. Am. Chem. Soc.* **52**, 3167–3176 (1930). (2) Rambaud, *Bull. soc. chim.* (5) **1**, 1340 (1934). (3) Rambaud, *Bull. soc. chim.* (5) **1**, 1348 (1934) (4) Backer, Benninga, *Rec. trav. chim.* **55**, 610 (1936). (5) Lespieau, *Bull. soc. chim.* (3) **33**, 466–467 (1905). (6) Glattfeld, Rietz, *J. Am. Chem. Soc.* **62**, 976 (1940). (7) Rambaud, *Compt rend.* **197**, 769 (1933). (8) Berthet, *Bull. acad. roy. Belg*, *Classe sci* **27**, 212–228 (1941); *Cent* **1942**, I 2115–2116; *C.A.* **37**, 3400 (1943). (9) Braun, *J. Am. Chem. Soc.* **52**, 3176–3185 (1930).

3:2174 2,4,6-TRICHLORORESORCINOL



$C_6H_3O_2Cl_3$ Beil. VI-820, VI_1—, VI_2—

M.P. 83° (1) (2) (3) (4)

Colorless cryst. from hot aq. (2). — C̄ is spar. sol. cold aq.; eas. sol. alc., ether. C̄ sublimes but with appreciable decompn.

[For prepn. of C̄ from resorcinol (1,3-dihydroxybenzene) (1:1530) with Cl_2 in aq. (4), AcOH (3) (2), or $CHCl_3$ (2), or with SO_2Cl_2 (excess) (4) or with dichlorourea (1), see indic. refs.]

[For formn. of C̄ from 2,4,4,6,6-pentachlorocyclohexen-1-dione-3,5 ("pentachlororesorcinol") [Beil. VII-572, VII_1-(323)] by reduction with sulfite (2) (5) or $SnCl_2$ (2) see

indic. refs.; from 2,2,4,4,5,6,6-heptachlorocyclohexanedione-1,3 ("heptachlorodihydroresorcinol") [Beil. VII-555] by similar reduction see (6).]

[$\bar{C}$ on oxidn. with alk. $K_3Fe(CN)_6$ gives (7) a yel. prod., m.p. 60°.]

$\bar{C}$ in not too dilute aq. soln. with $FeCl_3$ gives on warming a wine-red color (4).

—— **2,4,6-Trichlororesorcinol dimethyl ether:** unreported. [A prod. of m.p. 174° which may have this structure has been reported by indirect means (8).]

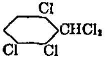
—— **2,4,6-Trichlororesorcinol diethyl ether:** unreported.

Ⓓ **2,4,6-Trichlororesorcinol diacetate:** cryst. from alc., m.p. 116° (2).

Ⓓ **2,4,6-Trichlororesorcinol dibenzoate:** pr. from alc., m.p. 133° (4). [From $\bar{C}$ with BzCl on htg. (4).]

3:2174 (1) Likhosherstov, *J. Gen. Chem.* (*U.S.S.R.*) **3**, 164–171 (1933); *Cent.* **1934**, I 1876; *C.A.* **28**, 1675 (1934). (2) Zincke, Rabinowitsch, *Ber.* **23**, 3776–3777 (1890). (3) Benedikt, *Monatsh.* **4**, 224–226 (1883). (4) Reinhard, *J. prakt. Chem.* (2) **17**, 336–341 (1878). (5) Claasen, *Ber.* **11**, 1441 (1878). (6) Zincke, Rabinowitsch, *Ber.* **24**, 913 (1891). (7) Stenhouse, Groves, *Ber.* **13**, 1307 (1880). (8) Ciamician, Silber, *Ber.* **24**, 2979–2980 (1891).

3:2178 2,3,6-TRICHLOROBENZAL (DI)-CHLORIDE $C_7H_3Cl_5$ Beil. S.N. 466
(2,3,6-Trichlorobenzylidene (di)-chloride)



M.P. 83° (1) **B.P. 145–150° at 12 mm. (1)**

Colorless ndls. from MeOH.

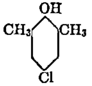
[For prepn. of $\bar{C}$ (81% yield) from 2,3,6-trichlorobenzaldehyde (3:2287) with PCl_5 see (1).]

Note that $\bar{C}$ depresses the m.p. (86–87°) of the corresp. aldehyde (3:2287).

[For study of rate of hydrolysis of $\bar{C}$ see (1).]

3:2178 (1) Asinger, Lock, *Monatsh.* **62**, 338 (1933).

3:2180 4-CHLORO-2,6-DIMETHYL-PHENOL C_8H_9OCl Beil. S.N. 529
(5-Chloro-*m*-2-xylenol)



M.P. 83° (1)

[For prepn. of $\bar{C}$ from 4-chloro-2,6-dimethylphenol (*vic-m*-xylenol) (1:1425) by chlorination with SO_2Cl_2 in AcOH (100% yield) see (1).]

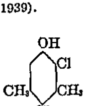
[For study of bactericidal action of $\bar{C}$ see (1).]

—— **4-Chloro-2,6-dimethylphenyl acetate:** unreported.

—— **4-Chloro-2,6-dimethylphenyl benzoate:** unreported.

3:2180 (1) Heicken, *Angew. Chem.* **52**, 264–265 (1939).

3:2182 2,4-DICHLORO-3,5-DIMETHYL-PHENOL $C_8H_8OCl_2$ Beil. VI—
(2,4-Dichloro-*m*-5-xylenol) VI_1—
VI_2-(464)



M.P. 83° (1)

Cryst. from lgr.

[For prepn. of C̄ from 4-chloro-3,5-dimethylphenol (2-chloro-*m*-5-xylenol) (3:3505) by chlorination with *N*-chloroacetamide see (1).]

The nitration of C̄ has not been reported, and the expected 6-nitro-2,4-dichloro-3,5-dimethylphenol is unknown

[For conversion of C̄ to various ethers see (1).]

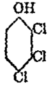
Ⓓ **2,4-Dichloro-3,5-dimethylphenol methyl ether:** m.p. 82° (1).

Ⓓ **2,4-Dichloro-3,5-dimethylphenol ethyl ether:** m.p 53° (1).

Ⓓ **2,4-Dichloro-3,5-dimethylphenyl *p*-nitrobenzyl ether:** m.p. 157° (1).

3:2182 (1) Jones, *J. Chem. Soc.* **1941**, 275

3:2185 2,3,4-TRICHLOROPHENOL $C_6H_3OCl_3$ Beil. VI —
VI_1—
VI_2-(179)



M.P. 83.5° (1) (6)
80–81° (2)
79° (3)

Ndls. from pet. eth. (1) (3). — Volatile with steam (1). — Ionization const. at 25° is 2.5×10^{-8} (6); C̄ is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 1,2,3-trichlorobenzene (3:0990) via nitration, reduction, and use of diazo reaction see (1) (4); from barium 3-chlorophenol-6-sulfonate by htg. with 80% H_2SO_4 see (3); by chlorination of 3,4-dichlorophenol see (2).]

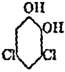
C̄ treated with Br_2/aq. in excess yields on pptn. with more aq. 6-bromo-2,3,4-trichlorophenol, pl. from lt. pet., m.p. 84–85° (5).

C̄ treated with $(CH_3)_2SO_4$ + aq. NaOH yields the methyl ether, 2,3,4-trichloroanisole, pr. from alc., m.p. 69.5° (3).

Ⓓ **2,3,4-Trichlorophenyl benzoate:** m.p. 143° (2); 141° (4).

3:2185 (1) Tiessens, *Rec. trav. chim.* **50**, 112–113 (1931). (2) Groves, Turner, Sharp, *J. Chem. Soc.* **1929**, 523. (3) Hodgson, Kershaw, *J. Chem. Soc.* **1930**, 1421. (4) Holleman, *Rec. trav. chim.* **39**, 743 (1920). (5) Fox, Turner, *J. Chem. Soc.* **1930**, 1863. (6) Tiessens, *Rec. trav. chim.* **48**, 1066–1068 (1929).

3:2192 3,5-DICHLOROCATECHOL $C_6H_4O_2Cl_2$ Beil. VI - 783
(3,5-Dichloropyrocatechol) VI_1—
VI_2—



M.P. 83–84° (1)

Colorless cryst. — Very eas. sol. hot, spar. sol. cold, aq.

[For prepn. of C̄ from 3,5-dichloro-2-hydroxybenzaldehyde (3,5-dichlorosalicylaldehyde) (3:2637) with H_2O_2 in alk. soln. see (1).]

C̄ reduces $NH_4OH/AgNO_3$ (1).

C̄ with $FeCl_3$ gives green color turning violet on addn. of $NaHCO_3$ (1).

—— **3,5-Dichloropyrocatechol diacetate:** unreported.

—— **3,5-Dichloropyrocatechol dibenzoate:** unreported.

3:2192 (1) Dakin, *Am. Chem. J.* **42**, 458–459 (1909).

tion and use of Cu_2Cl_2 reaction (1), or from 4-chloro-2,3-dimethylaniline (6-chloro-o-3-xylidine) (1) via diazotization and hydrolysis (70% yield (1)), see indic. refs.]

[For studies of bactericidal action of C̄ see (2) (3) (4).]

C̄ *with* Cl_2 *in lt. pet. does not* (1) *give a trichloro derivative but is decomposed.*

The nitration of C̄ has not been reported and neither of the corresp. mononitro derivs. nor the dinitro deriv. is known.

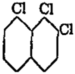
—— 4-Chloro-2,3-dimethylphenyl acetate: unreported.

Ⓓ 4-Chloro-2,3-dimethylphenyl benzoate: *m.p.* 102° (1).

3:2218 (1) Hinkel, (2) Heicken, *Angew.* *Chem.* 52, 203–205 ... 46, 296–301 (1933). (4) Lockemann, H... 51–71 (1939); *C.A.* 34, 2534 (1940).

3:2220 1,2,8-TRICHLORONAPHTHALENE

$C_{10}H_5Cl_3$ Beil. V-545 V_1— V_2—



M.P. 84° (1)
83° (2)

Ndls. from alc.

[For prepn. of C̄ from 8-chloro-1-nitronaphthalenesulfonic acid-2 [Beil. XI-187] (3), from 7,8-dichloronaphthol-1 (3:2635) (2), or from 1,2-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1), each with PCl_5, see indic. refs.]

[C̄ treated with $ClSO_3H$ in CS_2 and prod. conv. to potassium salt yields (1) potassium 1,2,8-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 105° (1)).]

3:2220 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 252. (2) Armstrong, Wynne, *Chem. News* 71, 253 (1895). (3) *Cleve, Chem. Ztg.* 17, 398 (1893).

3:2240 β-CHLOROACRYLIC ACID

$C_3H_3O_2Cl$ Beil. II - 400 II_1-(186) II_2—

H.C.Cl ‖ H.C.COOH (*cis*)   Cl.C.H ‖ H.C.COOH (*trans*)

M.P. *trans* 85–86° (1)
84–85° (2)
M.P. *cis* 63–64° (1)

[For prepn. of mixt. of *cis* and *trans* forms of C̄ from propiolic acid (acetylenecarboxylic acid) [Beil. II-477, II_1-(208), II_2-(449)] by htg. with conc. HCl (yield: *cis* 34%, *trans* 18% (1)) (3) (the *cis* is sepd. from *trans* by means of the lesser soly. in alc. of its potassium salt (1)), see indic. refs.; for prepn. of *trans* C̄ from β-chloropropionic acid (3:0460) by loss of HCl on passing its vapor over $BaCl_2$ at 280–300° see (4); from ethyl β,β-dichloropropionate with 3 moles alc. KOH see (5); from chloralide (3:3510) in alc. by protracted treatment with Zn + HCl see (2) (5).]

The *cis* isomer of C̄ on htg. in a s.t. at 125° for 15 hrs. is partially conv. (1) to the *trans* isomer.

C̄ (both forms) readily reduces $KMnO_4$ in the cold (1).

[C̄ on htg. with 5 pts. 40% HCl in s.t. at 80–85° for 35–40 hrs. yields (5) α,β-dichloropropionic acid (3:0855), m.p. 56° (5).]

[C̄ on esterification with EtOH yields ethyl β-chloroacrylate, b.p. 143–145° (2), 146° (6).]

3:2240 (1) Backer, Beute, *Rec. trav. chim.* **54**, 167–170 (1935). (2) Wallach, *Ann.* **193**, 28–34 (1878). (3) Bandrowski, *Ber.* **15**, 2702 (1882). (4) I.G., French 697,311, Jan 15, 1931; *Cent.* **1931**, I 2934. (5) Otto, *Ann.* **239**, 261–272 (1887). (6) Pinner, Bischoff, *Ann.* **179**, 88 (1875).

3:2265 α,β-DICHLOROACRYLIC ACID $C_3H_2O_2Cl_2$ Beil. II - 401 II₁-(186) II₂—

CH=C—COOH
| |
Cl Cl

M.P. 85–86° (1) (2) (3) (5) (6) (7) **Neut. Eq. 141**
87–88° (4)

Monoclinic (5) pr. (from $CHCl_3$ (5)); cryst. from pet. eth. (4) or CS_2 (7). — Eas. sol. aq, alc., ether (2) (4), $CHCl_3$ (2); *spar. sol. in cold (1) but eas sol. in hot C_6H_6, CS_2 or pet.* eth. (2). — Rapidly volatilizes in air (2) or on warming (4). — May be purified by melting with a *little* aq. (2).

Although two geom. isomers are possible only one is known.

[For prepn. from various sources see Beil. II-401, Beil II₁-(186), and (3).]

Salts: $Ag\bar{A}$, pptd. in fine ndls from even dil. aq solns. of $\bar{C}$ on addn. of $AgNO_3$; can be recrystd. from hot aq. (1) (2) (4) (6); Ag content = 43.54%; $Ba\bar{A}_2\,H_2O$, sol. in 16 pts. cold aq (1) (2) (4) (6); $Ca\bar{A}_2\,3H_2O$, extremely sol. aq., loses cryst. aq. at 80° (1) (2); $K\bar{A}$, quite sol. even in cold aq. but may be obtained in long slender anhyd. ndls. from conc. solns. (1) (2).

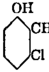
$\bar{C}$ in $CHCl_3$ does not add Br_2 (2), but $\bar{C}$ on htg. (in s t.) with 1 mole Br_2 at 100° gives (9) α,β-dibromo-α,β-dichloropropionic ac. [Beil. II-259], pr. from CS_2 or $CHCl_3$, m.p. 94–95° (9).

$\bar{C}$ is *not* decomposed by excess boil. $Ba(OH)_2$ (7).

$\bar{C}$ with thionyl chloride yields (7) α,β-dichloroacrylyl chloride, b.p. 145–146°, n_D^{17} = 1.5288, *which is only slowly hydrolyzed by aq but which on cautious addn. to conc.* NH_4OH yields α,β-dichloroacrylamide, cryst. from dil. alc, m.p. 134° (7), 132° (10).

3:2265 (1) Bennett, Hill, *Ber.* **12**, 655–657 (1879). (2) Hill, *Am Chem. J.* **3**, 167–172 (1881/2). (3) Klebansky, Wolkenstein, Orlowa, *J. prakt. Chem.* **145**, 12–13 (1936). (4) Zincke, *Ber.* **24**, 918 (1891). (5) Melville, *Am Chem. J.* **4**, 174–176 (1882/3). (6) Ciamician, Silber, *Ber.* **16**, 2392 (1883). (7) Prins, *J. prakt. Chem.* (2) **89**, 420 (1914). (8) Prins, *Rec. trav. chim.* **56**, 780–781 (1937). (9) Hill, Maberry, *Ber.* **14**, 1679–1680 (1881); *Am. Chem. J.* **4**, 267–270 (1882/3). (10) Prins, Ger. 261,689, July 2, 1913; *Cent.* **1913**, II 394.

3:2280 3-CHLORO-2-METHYLPHENOL (3-Chloro-o-cresol) C_7H_7OCl Beil. VI - 350 VI₁— VI₂—



M.P. 86° (1) (2) (3) **B.P. 225° (2)**

Long white ndls. (from aq) (1) — Volatile with steam (2).

[For prepn. (75–86% yield) from 3-chloro-2-methylaniline [Beil. XII-836] see (1) (2); from 3-hydroxy-2-methylaniline [Beil. XIII-579] (45–50% yield) see (1).]

$\bar{C}$ on nitration (1) in AcOH with 100% HNO_3 at +10° yields mixt. of equal amts. of two mononitration products: 6-nitro-3-chloro-2-methylphenol [Beil. VI-366], volatile with steam, yel. cryst. from alc., m p. 64 5° (1), and 4-nitro-3-chloro-2-methylphenol [Beil. VI-367], not volatile with steam, cryst. from aq., m p. 135° (1).

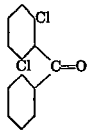
$\bar{C}$ on nitration (4) with 3 pts. HNO_3 (D = 1.48) at 0° gives a dinitro compd., 4,6-dinitro-3-chloro-2-methylphenol, long yel. ndls. from dil. alc., m.p. 82–83° (4); acetyl deriv., m p. 95° (4).

C̄ in alk. soln. coupled with diazotized *p*-nitroaniline yields (1) 3-chloro-2-methyl-6-(*p*-nitrobenzene-azo-)phenol [Beil. XVI-132], cryst. from 50% alc., m.p. 230°.

C̄ in 3 pts. 20% NaOH shaken with 1 pt. $(CH_3)_2SO_4$, distilled with steam, gives 3-chloro-2-methylanisole [Beil. VI-359], b.p. 213.5° (2).

3:2280 (1) Noelting, *Ber.* **37**, 1019–1021 (1904). (2) Ullmann, Panchaud, *Ann.* **350**, 112–113 (1906). (3) Zincke, *Ann.* **417**, 207 (1918). (4) Zincke, *Ann.* **417**, 234–235 (1918).

3:2285 2,6-DICHLOROBENZOPHENONE (2,6-Dichlorophenyl phenyl ketone) $C_{13}H_8OCl_2$ Beil. S.N. 652



M.P. 86° (1)

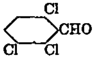
Colorless cryst. (from alc. (1)).

C̄ does not react with the usual ketone reagents (1).

C̄ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (1) BzOH (1:0715)(96% yield) and *m*-dichlorobenzene (3:5960).

3:2285 (1) Lock, Rödiger, *Ber.* **72**, 869 (1939).

3:2287 2,3,6-TRICHLOROBENZALDEHYDE $C_7H_3OCl_3$ Beil. VII-238 VII_1—



M.P. 86–87° (1)
86° (2) (3)

Colorless ndls. from lgr.

[For prepn. of C̄ from 3-amino-2,6-dichlorobenzaldehyde by diazotization and use of Cu_2Cl_2 reaction see (1) (2).]

C̄ with PCl_5 gives (81% yield (4)) 2,3,6-trichlorobenzal (di)chloride (3:2178), m.p. 83°; note that this prod. depresses m.p. of C̄.

C̄ with 50% aq. KOH at 100° for 5 hrs. under N_2 undergoes cleavage of the aldehyde group giving (88% yield (3)) 1,2,4-trichlorobenzene (3:6420) and the corresp. potassium formate.

C̄ with anhydrous NaOAc + Ac_2O on htg. (Perkin synthesis) gives (64–68% yield (5)) 2,3,6-trichlorocinnamic acid, cryst. from AcOH, m.p. 189°.

[C̄ with MeMgI in dry ether, followed by usual hydrolysis, gives (85% yield (2)) methyl-2,3,6-trichlorophenyl-carbinol, m.p. 87–88°, b.p. 149–155° at 11 mm. (corresp. benzoate, m.p. 106.5°).]

—— **2,3,6-Trichlorobenzaldoxime:** unreported.
—— **2,3,6-Trichlorobenzaldehyde phenylhydrazone:** unreported.
—— **2,3,6-Trichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.
—— ***2,3,6-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone:*** unreported.

3:2287 (1) Geigy [illegible] II 263–264; *C.A.* 2, 3000 (1908).
(2) Lock, Böck, *B* [illegible] *atsh.*
62, 338 (1933).

3:2290 PENTACHLOROBENZENE

C_6HCl_5 Beil. V - 205
V_1-(113)
V_2-(157)

M.P. 87° (1) (2)
86–87° (3) (4)
86° (4) (5) (6) (7) (17)
85–86° (8) (9) (10)
85° (11) (12) (13)
84–85° (14)
84° (15) (16)

B.P. 275–277° (10)

Long colorless ndls from alc.; volatile with steam; sublimes readily. — Almost insol. cold alc., apprec. sol. boilg. alc.; eas. sol. ether, C_6H_6, $CHCl_3$, CCl_4, or CS_2; spar. sol. conc. HNO_3.

[For prepn. of C̄ from nonachlorobenzophenone-*o*-carboxylic acid [*o*-(pentachlorobenzoyl)-tetrachlorobenzoic acid] [Beil. X_1-(358)] by htg with 10 pts conc. H_2SO_4 at 200–250° for ½ hr. (simplest prepn. of pure C̄) see (12); for formn of C̄ from 2,3,4,5,6-pentachloroacetophenone (6) or 2,3,4,5,6-pentachlorobenzophenone (11) by KOH/NaOH fusion see indic refs, from 2,3,4,5,6-pentachlorobenzaldehyde (3:4892) (2) by htg. with 50% aq KOH 5 hrs at 100° (88% yield) see (2).]

[For prepn of C̄ from 2,3,5,6-tetrachloroaniline (7) via diazotization and use of Cu_2Cl_2 reactn. see (7), from 2,3,5-trichloro-*p*-phenylenediamine via tetrazotization in AcOH with nitrosylsulfuric acid and use of Cu_2Cl_2 reactn (80% yield) see (3).]

[For formn. of C̄ from benzene with Cl_2 (7), or Cl_2 + cat (20), or Cl_2 in pres. of I_2 (18), or $AlCl_3$ (19) see indic refs; from chlorobenzene with Cl_2 + Cu at 200° see (21); from 1,3,5-trichlorobenzene (3:1400) with Cl_2 + Al/Hg see (17); from all three tetrachlorobenzenes with Cl_2 + Al/Hg see (17); from 1,2,4,5-tetrachlorobenzene (3:4115) in $SOCl_2$ or CCl_4 with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 see (8) (note that under these circumstances *p*-dichlorobenzene (3:0980) gives a mixt. of tetra and hexachlorobenzenes (8) (22)); from lower chlorinated derivs. of benzene by htg. with $FeCl_3$ see (5); from diphenyl sulfone with Cl_2 in sunlight followed by treat. with alc. KOH see (13) (23); from tetrachlorobenzyl chloride with Cl_2 see (16); from acet-*N*-nitro-2,3,5,6-tetrachloroaniline on htg. in toluene or from parent base on attempted acetylation see (15); from trichloroethylene (3:5170) at 700° see (9); from iodopentachlorobenzene with MeOH/NaOH see (1).]

[For formn. of C̄ from various chlorine addition products derived from *o*-dichlorobenzene (3:6055) (4), *m*-dichlorobenzene (3:5960) (4), *p*-dichlorobenzene (3:0980) (4), 1,2,4,5-tetrachlorobenzene (3:4115) (24), and even C̄ itself (25) see indic refs.]

[C̄ with liq. Cl_2 in s.t. in sunlight adds 2 Cl_2 with considerable sluggishness yielding (26) (25) a mixt of two stereoisomeric nonachlorocyclohexenes.]

[C̄ with fumg. H_2SO_4 gives on protracted htg (27) a red dyestuff, sol. in alk. with deep red color.]

[C̄ with $N/2$ NaOMe in MeOH in s.t. at 180° for 7½ hrs. gives (7) 2,3,5,6-tetrachlorophenol, m.p 115° (7) (benzoate, m.p. 136° (28)), accompanied by a small amt. 2,3,4,5-tetrachlorophenol, itself not obtd. pure but yielding (28) a benzoate of m.p. 110° (28). — [For further study of actn. of MeOH/NaOH on C̄ see (29) (30).]

C̄ on nitration, e g, with 7–8 wt. pts. HNO_3 (D = 1.52) at 100° for 1 hr. (7), gives (7) (9) (18) (31) pentachloronitrobenzene [Beil. V-247], ndls. from alc., tbls. from CS_2, m p 146° (9) (18) (31), 143° (7); note that since C̄ is spar. sol. in conc. HNO_3 any unchanged material may separate with the crude prod. (31). — [This pentachloronitrobenzene with

$N/10$ NaOMe in MeOH boiled for 8 hrs. loses NO_2 instead of Cl yielding (31) methyl pentachlorophenyl ether (pentachloroanisole), m.p. 104–105° (31); cf. also under pentachlorophenol (3:4850).]

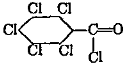
3:2290 (1) van der Linden, *Rec. trav. chim.* **55**, 285 (1936). (2) Lock, *Ber.* **66**, 1533 (1933). (3) Schoutissen, *J. Am. Chem. Soc.* **55**, 4539–4540 (1933). (4) van der Linden, *Ber.* **45**, 411–418 (1912). (5) Thomas, *Compt. rend.* **126**, 1212 (1898). (6) Lock, Böck, *Ber.* **70**, 925 (1937). (7) Holleman, van der Hoeven, *Rec. trav. chim.* **39**, 745–746, 749 (1920). (8) Silberrad, *J. Chem. Soc.* **121**, 1020–1021 (1922). (9) Nicodemus, *J. prakt. Chem.* (2) **83**, 319 (1911). (10) Ladenburg, *Ann.* **172**, 344 (1874).

(11) Lock, Rödiger, *Ber.* **72**, 870 (1939). (12) Eckert, Steiner, *Monatsh.* **36**, 183 (1915); *Ber.* **47**, 2629 (1914). (13) Otto, *Ann.* **154**, 185 (1870). (14) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 434 (1932). (15) Peters, Rowe, Stead, *J. Chem. Soc.* **1943**, 372. (16) Beilstein, Kuhlberg, *Ann.* **152**, 247–248 (1869). (17) Cohen, Hartley, *J. Chem. Soc.* **87**, 1366 (1905). (18) Jungfleisch, *Ann. chim.* (4) **15**, 283–287 (1868). (19) Mouneyrat, Pouret, *Compt. rend.* **127**, 1028 (1898). (20) Moose, Malowan (to Swann Research, Inc.), U.S. 2,010,495, Aug. 6, 1935; *Cent.* **1936**, 2984; *C.A.* **29**, 6330 (1935).

(21) Tei, Komatsu, *Mem. Coll. Sci., Kyoto Imp. Univ.* **A-10**, 325–330 (1927); *Cent.* **1928**, I 2370. (22) Roberts and Co., & Silberrad, Brit. 193,200, March 15, 1923; *Cent.* **1925**, I 904. (23) Otto, Ostrop, *Ann.* **141**, 107–108 (1867). (24) van der Linden, *Rec. trav. chim.* **55**, 425–427 (1936). (25) van der Linden, *Rec. trav. chim.* **55**, 569–570 (1936). (26) van der Linden, *Rec. trav. chim.* **55**, 322 (1936). (27) Istrati, *Bull. soc. chim.* (2) **48**, 36–41 (1887). (28) Holleman, *Rec. trav. chim.* **40**, 318–319 (1921). (29) de Crauw, *Rec. trav. chim.* **50**, 787 (1931). (30) van der Linden, *Rec. trav. chim.* **57**, 787 (1938).

(31) Berckmans, Holleman, *Rec. trav. chim.* **44**, 857–858 (1925).

3:2295 PENTACHLOROBENZOYL CHLORIDE



C_7OCl_6 Beil. S.N. 938

M.P. 87° (1)

Colorless tbls. from hot alc.

[For prepn. of C̄ from *unsym.*-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVIII₁-(484)] on htg. at 300° in pres. of Cl_2 see (1).]

C̄ during protracted htg. loses CO yielding (1) hexachlorobenzene (3:4939) (this type of decompn. is generally facilitated by $AlCl_3$ although in this case this aspect has not been reported).

C̄ with MeOH on refluxing for 30 hrs. gives (1) methyl pentachlorobenzoate m.p. 97° (1); note that esterification is slow and that C̄ can be recrystallized from EtOH without change.

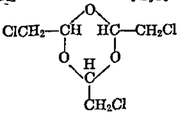
C̄ on hydrolysis with alc. KOH, followed by acidification, yields (1) pentachlorobenzoic acid (3:4910).

3:2295 (1) Kirpal, Kunze, *Ber.* **62**, 2104–2105 (1929).

3:2300 TRICHLOROPARALDEHYDE

(Chloroacetaldehyde trimer; 2,4,6-*tris*-(chloromethyl)-trioxane-1,3,5)

$C_6H_9O_3Cl_3$ Beil. XIX - 386; XIX_1-(807)



M.P. 87–87.5° cor. (1) **B.P. 142–144° at 10 mm. (2)**
140° at 10 mm. (1)

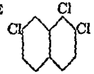
Colorless ndls. from ether; insol. aq., spar. sol. cold alc., eas. sol. hot alc. or in ether.

[For prepn. of C̄ from chloroacetaldehyde (3:7212) (or its hydrate) with ½ vol. cold conc. H_2SO_4 see (1) (3) (4).]

C̄ on distn. at ord. press. (1) (2) (3) (4) depolymerizes to monomeric chloroacetaldehyde (3:7212), b.p. 85°.

3:2300 (1) Natterer, *Monatsh.* **3**, 459–464 (1882). (2) Späth, *Monatsh.* **36**, 6–7 (1915). (3) Helferich, Speidel, *Ber.* **54**, 2634–2635 (1921). (4) Lespieau, *Bull. soc. chim.* (4) **43**, 200–201 (1928).

3:2325 1,2,7-TRICHLORONAPHTHALENE $C_{10}H_5Cl_3$ Beil. V - 545 V_1-(263) V_2—



M.P. 88° also 84° (1) (2)
(*See Text.*)

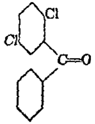
C̄ shows the double m.p. behavior indicated also for several of its isomers, e.g., 1,2,3-isomer (3:2125), 1,2,5-isomer (3:1930), 1,3,8-isomer (3:2420), 1,4,6-isomer (3:1625).

[For prepn. of C̄ from 1-chloro-7-sulfonaphthylamine-2 [Beil. XIV-765] via diazotization and use of Cu_2Cl_2 reactn. see (1) (2); from 1,2-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-184] (2) (3), from 1-chloro-7-nitronaphthalenesulfonyl chloride-2 [Beil XI-188] (4), from 2-chloro-1-nitronaphthalenesulfonyl chloride-2 [Beil. XI-189] (5) (2), or from 1-chloronaphthalene-2,7-*bis*-(sulfonyl chloride) [Beil. XI-217] (2), each with PCl_5 as directed, see indic. refs.]

[C̄ treated with $ClSO_3H$ in CS_2 and reactn prod. conv. to sodium salt as directed (1) yields sodium 1,2,7-trichloronaphthalenesulfonate-X (corresp. sulfonyl chloride, m.p. 176° (1)).]

3:2325 (1) Turner, Wynne, *J. Chem. Soc* **1941**, 247, 252. (2) Armstrong, Wynne, *Chem. News* **71**, 253–254 (1895). (3) Armstrong, Wynne, *Chem. News* **59**, 189 (1889). (4) Cleve, *Chem. Ztg.* **17**, 398 (1893). (5) Cleve, *Ber.* **25**, 2486–2487 (1892).

3:2340 2,5-DICHLOROBENZOPHENONE (2,5-Dichlorophenyl phenyl ketone) $C_{13}H_8OCl_2$ Beil. S.N. 652



M.P. 88° (1) (3)
85–86° (2)

Cryst. (from alc. (1)). — C̄ does not form a $NaHSO_3$ cpd. (1).

[For prepn. (20% yield (1)) from *p*-dichlorobenzene (3:0980) + BzCl (3:6240) + $AlCl_3$ see (1) (2).]

C̄ fused for 3 hrs. at 200° with a mixt. of KOH + NaOH gives (3) *p*-dichlorobenzene (3:0980) (65% yield (3)) and BzOH (1:0715) (91% yield (3)).

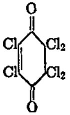
C̄ on oxidn. with $KMnO_4$ soln. yields (1) 2,5-dichlorobenzoic ac. (3:4340), m p. 150° (1).

Ⓓ 2,5-Dichlorobenzophenone oxime: from C̄ in alc. on htg. with $NH_2OH.HCl$ + $BaCO_3$ for 3 days (10% yield (1)); m p. 135° (on rapid htg.), 207° (on slow htg.) (1). [This

oxime upon Beckmann rearr. with 10 pts. conc. H_2SO_4 at 100° for 1 hr. gives benz-2,4-dichloroanilide, m.p. 122° (1).]

3:2340 (1) de Crauw, *Rec. trav. chim.* **50**, 767–768 (1931). (2) Ganzmüller, *J. prakt. Chem.* **138**, 311–312 (1933). (3) Lock, Rödiger, *Ber.* **72**, 869 (1939).

3:2360 2,3,5,5,6,6-HEXACHLORO-CYCLOHEXENE-2-DIONE-1,4



$C_6O_2Cl_6$ Beil. VII - 574 VII₁—

M.P. 89°	(1)	B.P. 275–285° dec.	(1)
86–87°	(2)	182–185° at 45–50 mm.	(1)

Cryst. (from ether/pet. ether). — Lachrymatory odor. — Eas. volatile with steam; on distn. at atm. press. dec. into chloranil (3:4978) and Cl_2. — Eas. sol. ether, $CHCl_3$; fairly eas. sol. alc., C_6H_6, lgr.; insol. aq.

[For prepn. from chloranil (3:4978) by treatment with MnO_2 + conc. HCl in s.t. for 10 hrs. at 180° see (1); from *p*-aminophenol hydrochloride in AcOH on treatment with Cl_2 see (1).]

[For use of C̄ as fungicide see (3).]

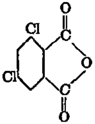
C̄ with KI in AcOH yields (1) chloranil (3:4978). — C̄ on reduction with $SnCl_2$ yields (1) tetrachlorohydroquinone (3:4941).

C̄ on shaking with 10% aq. NaOH slowly dissolves with decompn. into dichloromaleic acid, trichloroethylene, and HCl (1).

Ⓓ 3,5,5,6,6-Pentachlorocyclohexanetrione-1,2,4-anil-2 [Beil. XII-212]: in alm. 100% yield from C̄ (1 pt.) in AcOH (5 pts.) htd. ½–¾ hr. at 100° with aniline (1 pt.), then cooling; red cryst., m.p. 144 (1). [This prod. is stable to conc. HCl but on stdg. with 6–8 pts. 10% aq. NaOH reacts suddenly with evoln. of ht. and odor of carbylamine; after dilution and filtration, acidification of the filtrate ppts. 1-phenyl-3,5,6-trichloropyridone-4-carboxylic acid-2 [Beil. XXII-298], m.p. 245° dec. (1)]

3:2360 (1) Zincke, Fuchs, *Ann.* **267**, 15–24 (1892). (2) Theilacker, *Ber.* **71**, 2069 (1938). (3) Ladd (to U.S. Rubber Co.), U.S. 2,362,565, Nov. 14, 1944; *C.A.* **39**, 2832 (1945).

3:2375 3,5-DICHLOROPHTHALIC ANHYDRIDE



$C_8H_2O_3Cl_2$ Beil. XVII - 483 XVII₁—

M.P. 89° (1) (2)

[*See also 3,5-dichlorophthalic acid* (3:4580).]

Ndls. from lgr.; eas. sol. ether, C_6H_6, $CHCl_3$.

[For prepn. from 3,5-dichlorophthalic acid (3:4580) by htg. [illegible] AcCl (1), see indic. refs.; from 3,5-disulfophthalic [illegible] (2) with [illegible] at 180° see (2).]

C̄ htd. with resorcinol + a drop of conc. H_2SO_4, then dislvd. in alk. and diluted, gives brilliant greenish fluorescence (1).

[C̄ with hydroquinone (1:1590) + $AlCl_3$ + NaCl htd. at 200–220° for 40 min. gives (3) 5,7-dichloro-1,4-dihydroxyanthraquinone (5,7-dichloroquinizarin), red ndls. from xylene, m.p. 231–232° (3).]

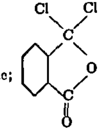
[C̄ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (4) 2,4-dichlorobenzoic acid (3:4560) and/or 3,5-dichlorobenzoic acid (3:4840).]

C̄ on melting and treatment with dry NH_3 gas yields (1) 3,5-dichlorophthalimide [Beil. XXI-504], yel. ndls. from hot alc., m p. 208° (1); C̄ on htg. with 1 mole aniline until evoln. of gas stops gives (1) 3,5-dichlorophthalanil [Beil. XXI-504], yel ndls. from alc., m p. 150 0–150.5° (1).

C̄ is insol. in cold aq. but hydrolyzes on boilg ; C̄ on sapon. with standard alk. (Sap. Eq. = 108 5) followed by acidifn. yields 3,5-dichlorophthalic acid (3:4840) q.v.

3:2375 (1) Crossley, LeSueur, *J. Chem. Soc.* **81**, 1536–1537 (1902). (2) Waldmann, Schwenk, *Ann.* **487**, 293–294 (1931). (3) Waldmann, *J. prakt Chem.* (2) **130**, 99–100 (1931). (4) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934, *Cent.* **1934**, II 3047.

3:2395 *unsym.-o-*PHTHALYL DICHLORIDE (*unsym.-o-*Phthaloyl dichloride; 3,3-dichlorophthalide)



$C_8H_4O_2Cl_2$ Beil. IX - 805 XVII$_1$-(162)

[*See also sym.-o-phthalyl dichloride* (3:6900).]

M.P. 89°, (1)
88–89° (2)
88.5° (3) (5)
87–89° (4)
84° (6)

$D_4^{99\,5}$ = 1.3320 (6)
D_4^{90} = 1.351 (5)

Prisms from C_6H_6 (2), cryst. from pet. eth. (b p. 20–50°) (4). — C̄ is much less reactive but far more lachrymatory (7) than *sym*-*o*-phthalyl dichloride (3:6900). — The m.p. of C̄ is not sharp because of beginning of conversion to *sym.* isomer (4) (5), and C̄ shows progressive change of density when kept at 90° for 1 hr (5) — C̄ on distillation is converted to the *sym.* isomer and therefore shows b.p. of the latter; this change is accelerated by presence of $AlCl_3$ or $SnCl_4$ (1) (2) or by HCl. — C̄ should therefore be preserved in a desiccator over soda-lime (2). — For f.p./compn. diagram of C̄ with its *sym.* isomer see (3); the eutectic has m.p. +8° and conts 23% C̄.

[For prepn. of C̄ from *sym.-o-*phthalyl dichloride by htg with $AlCl_3$ at 100° for 8–10 hrs. (72% yield) see (4).]

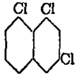
C̄ in anhydrous *formic* acid *reacts* below 40° evolving HCl + CO (7) (the *sym.* isomer reacts much more readily, even below 25° (7)).

C̄ on shaking at 0° with 10 vols. 7% aq. NH_4OH followed by acidification yields (1) (7) *o*-cyanobenzoic acid [Beil. IX-814, IX$_1$-(365)], m p 190° dec., converted by htg. to phthalimide, m.p. 228 5° u.c. [Exactly this same result is obtd. with the *sym* isomer.]

[For studies of rate of reactn. of C̄ with MeOH or with aniline see (2) (8).]

[For differentiation of C̄ from its *sym.* isomer by use of piperidinium *N*-piperidyldithiocarbamate (from piperidine + aq. + CS_2) see (6) (7).]

3:2395 (1) Scheiber, *Ber.* 46, 2308–2309 (1913). (2) Ott, *Ann.* 392, 273–276 (1912). (3) [illegible] 40, 81–92 (1919). (4) Ott, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 528–530 (1943); [illegible] (6) von Braun, Kaiser, *Ber.* [illegible] (8) Dann, Davies, Hambly, [illegible]

3:2420 1,3,8-TRICHLORONAPHTHALENE  $C_{10}H_5Cl_3$ Beil. V - 545
V_1—
V_2—

M.P. 89.5° (1)
89° (2)

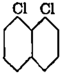
84° (1)
85° (2)
(*See text.*)

Ndls. from alc. in which it is eas. sol. — Note that $\bar{C}$ (like certain of its isomers) shows a peculiar characteristic; if the fused $\bar{C}$ in a m.p. tube is allowed to cool and withdrawn it solidifies to a translucent form which on immediate reheating shows m.p. 84–85° but if left for a time is conv. to an opaque mass which on htg. shows m.p. 89°.

[For prepn. of $\bar{C}$ from 1-chloronaphthalene-3,8-*bis*-(sulfonyl chloride) [Beil. XI-214] with PCl_5 see (1) (3); from 1-nitronaphthalene [Beil. V-553, V_1-(264)] with Cl_2 see (4) (2).]

[$\bar{C}$ treated with $ClSO_3H$ in CS_2 and prod. conv. to sodium salt yields (1) sodium 1,3,8-trichloronaphthalenesulfonate-5 (corresp. sulfonyl chloride, m.p. 127° (1)).]

3:2420 (1) Turner, Wynne, *J. Chem. Soc.* 1941, 247, 254. (2) Armstrong, Wynne, *Chem. News* 71, 255 (1895). (3) Armstrong, Wynne, *Chem. News* 61, 94 (1890). (4) Atterberg, *Ber.* 9, 926 (1876).

3:2435 1,8-DICHLORONAPHTHALENE  $C_{10}H_6Cl_2$ Beil. V - 544
V_1—
V_2-(446)

M.P. 89.0–89.5° (1)
88.5–89° (2)
88.5° (8)
88° (3) (4)
84–85° (7)
83° (5)
82.5–83.5° (11)
82° (10)

Cryst. from al[illegible] with steam [illegible]

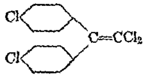
[For prepn. of [illegible] via [illegible]
ation and htg. [illegible] from [illegible]
XII-1256] via diazotization and use of Cu_2Cl_2 [illegible] 52% [illegible] see [illegible]
from 1,8-dinitronaphthalene [Beil. V-559, V[illegible]
naphthalenesulfonyl chloride-1 [Beil. XI-1[illegible]
see (4); from 4,5-dichloronaphthal[illegible]
of —SO_3H group at 230° see (9) (3); [illegible]
[Beil. XI-182] by htg. with 1% H_2SO_4 [illegible]

C̄ *htd. with HCl in s.t. at 250–290° rearranges (9) to 1,5-dichloronaphthalene (3:3200)*, m.p. 107°.

[C̄ in CS_2 treated with $ClSO_3H$ yields (10) 1,8-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp. sulfonyl chloride, m.p. 114° (10), corresp. sulfonamide, m p. 228° (10)).]

3:2435 (1) Hampson, Weissberger, *J. Chem. Soc.* **1936**, 394. (2) Weissberger, Sängewald, Hampson, *Trans. Faraday Soc.* **30**, 890 (1934). (3) Cleve, *Chem. Ztg.* **17**, 398 (1893). (4) Armstrong, Wynne, *Chem. News* **71**, 255 (1895). (5) Atterberg, *Ber.* **9**, 1732 (1876). (6) Atterberg, *Ber.* **10**, 548 (1877). (7) Bergmann, Hirshberg, *J Chem Soc.* **1936**, 334. (8) Krollpfeiffer, *Ann.* **430**, 198 (1923). (9) Armstrong, Wynne, *Chem News* **76**, 69–70 (1897). (10) Armstrong, Wynne, *Chem. News* **61**, 273–274 (1890)
(11) Woroshtzow, Koslow, *Ber.* **69**, 413 (1936).

3:2438 1,1-DICHLORO-2,2-*bis*-(*p*-CHLOROPHENYL)-ETHYLENE $C_{14}H_8Cl_4$ **Beil. S.N. 480**



M.P. 89° (1)
88–89° (2)
86–87° (3)

Colorless cryst. from alc.

[For prepn. of C̄ from 1,1,1-trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT") (3:3298) by elimination of 1 HCl with alc. KOH under reflux (1) for 10 hrs (3) or 15–20 min. (4) (*yields: almost 100% (4), 81% (3)) (for study of rate see (5)), or by htg. at 110–120° with* a trace of $FeCl_3$ or $AlCl_3$ (2), see indic. refs.; for prepn of C̄ from 1,1,1,2-tetrachloro-2,2-*bis*-(*p*-chlorophenyl)ethane (3:2477) by elimination of two adjacent chlorine atoms with Zn dust in boilg. abs alc. refluxed 8 hrs. (66% yield) see (3)]

C̄ on oxidn. with CrO_3/AcOH refluxed 4 hrs gives (*100% yield* (3)) *4,4'*-dichlorobenzophenone (3:4270), m.p. 144° (3).

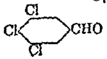
C̄ in boilg. $CHCl_3$ contg. a little PCl_3 with Cl_2 for 3 hrs. (but without special radiation) adds 1 mole halogen giving (*70% yield* (3)) *1,1,1,2-tetrachloro-2,2-bis-(p-chlorophenyl)*-ethane (3:2477), m.p. 91–92° (3).

C̄ with KOH in ethylene glycol refluxed 10–12 hrs gives (*almost 100%* yield (4)) 4,4'-dichlorodiphenylmethane (3:1057) *m.p.* 55°; but note that C̄ with excess $Ba(OH)_2 8H_2O$ in ethylene glycol refluxed 10–12 hrs. (4) or C̄ with alc KOH in s.t at 150–160° for 24 hrs. (7) gives (yields: 57% (7), 33% (4)) *di-(p-chlorophenyl)acetic acid* (3:4612), m.p. 166.0–166 5° u c. (4), 163–164° (7), *this acid undoubtedly* being the precursor which by loss of CO_2 with the above KOH gives the indicated prod.

C̄ with anhydrous $AlCl_3$ in large excess C_6H_6 does *not* (6) give *1,1,2,2-tetraphenylethane* (dif. from "DDT" (3:3298) q.v).

3:2438 (1) Zeidler, *Ber.* **7**, 1181 (1874). (2) ... **66**, 2005 (1944)
(3) Grummitt, Buck, Jenkins, *J. Am. Che*...
U.S. Pub. Health Repts. **60**, 66–71 (1945).
(6) Fleck, Haller, *J. Am. Chem. Soc.* **67**, 1...
Chem. Soc. **67**, 156 (1945).

3:2440 3,4,5-TRICHLOROBENZALDEHYDE $C_7H_3OCl_3$ **Beil. S.N. 635**



M.P. 90–91° (1)

Colorless ndls. from alc. — Somewhat sol. boilg. aq.; volatile with steam. — Eas. sol. in hot alc.; also in ether, acetone, C_6H_6, or $CHCl_3$; fairly sol. pet ether.

[For prepn. of C̄ from 4-amino-3,5-dichlorobenzaldehyde (1) by diazotization and use of Cu_2Cl_2 reaction (yield of crude C̄ 80%) see (1).]

C̄ on oxidn. with alk. $KMnO_4$ gives (1) 3,4,5-trichlorobenzoic acid (3:4920), m.p. 210°.

C̄ on mononitration, with abs. HNO_3 in cold, gives (86% yield crude (1)) 2-nitro-3,4,5-trichlorobenzaldehyde, m.p. 118.5–119° (corresp. phenylhydrazone, m.p. 229° dec.; corresp. *p*-nitrophenylhydrazone, m.p. 293–294° dec.; corresp. semicarbazone, m.p. 278–279° dec.).

—— *3,4,5-Trichlorobenzaldoxime:* unreported.

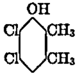
Ⓓ **3,4,5-Trichlorobenzaldehyde phenylhydrazone:** m.p. 147° (1).

—— **3,4,5-Trichlorobenzaldehyde *p*-nitrophenylhydrazone:** orange ndls. from nitrobenzene, m.p. 342° dec. (1).

Ⓓ **3,4,5-Trichlorobenzaldehyde semicarbazone:** cryst. from alc., m.p. 252–254° (rap. htg.), but after fusion resolidifies and remelts at 284–285° (1).

3:2440 (1) Van de Bunt, *Rec. trav. chim.* **48**, 131–137 (1929).

3:2442 5,6-DICHLORO-2,3-DIMETHYLPHENOL (4,5-Dichloro-*o*-3-xylenol)



$C_8H_8OCl_2$ Beil. VI —, VI_1—, VI_2-(454)

M.P. 90° (1)
[95° (2)]

Cryst. from lt. pet. — Volatile with steam.

[For prepn. of C̄ from 5,6-dichloro-2,3-dimethylaniline (4,5-dichloro-*o*-3-xylidine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of C̄ from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with quinoline at 170° for 30 min. (yield not stated) see (2).]

C̄ with Cl_2 in $CHCl_3$ does *not* give the expected 4,5,6-trichloro-2,3-dimethylphenol (3:4742) but instead (2) a tetrachloro deriv. (apparently containing a chlorinated methyl group), m.p. 127.5° (2).

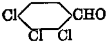
The nitration of C̄ has not been reported, and the expected 4-nitro-5,6-dichloro-2,3-dimethylphenol is unknown.

—— 5,6-Dichloro-2,3-dimethylphenyl acetate: unreported.

Ⓓ **5,6-Dichloro-2,3-dimethylphenyl benzoate:** m.p. 133° (1), 128° (2).

3:2442 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 2533. (2) Hinkel, *J. Chem. Soc.* **125**, 1850–1851 (1924). (3) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 1876–1877.

3:2445 2,3,4-TRICHLOROBENZALDEHYDE



$C_7H_3OCl_3$ Beil. VII - 238, VII_1—

M.P. 91° (1)
90° (2)

Ndls. from alc.

[For prepn. of C̄ from 2,3,4-trichlorobenzal (di)chloride (3:2212) in 58% yield by hydrolysis with fumg. H_2SO_4 as directed see (2).]

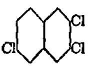
C̄ on oxidn. with $KMnO_4$ gives (1) 2,3,4-trichlorobenzoic acid (3:4810), m.p. 186–187°.

C̄ with anhydr. NaOAc + Ac_2O on htg. (Perkin synthesis) gives (2) 2,3,4-trichlorocinnamic acid [Beil. IX-597], m.p. 185°.

—— **2,3,4-Trichlorobenzaldoxime:** unreported.
—— **2,3,4-Trichlorobenzaldehyde phenylhydrazone:** unreported.
—— **2,3,4-Trichlorobenzaldehyde *p*-nitrophenylhydrazone:** unreported.
—— **2,3,4-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone:** unreported.

3:2445 (1) Nicodemus, *J. prakt. Chem.* (2) **83**, 319 (1911). (2) Seelig, *Ann.* **237**, 149–151 (1887).

3:2455 2,3,6-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V - 546
V_1—
V_2-(446)

M.P. 91° (1)
90.5–91° (2)

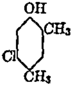
[For prepn. of C̄ from 3,6-dichloronaphthalenesulfonyl chloride-2 [Beil. XI-182] (1) (2), from 3-chloronaphthalene-2,7-*bis*-(sulfonyl chloride) [Beil. XI-217] (1) (3), or from 3-chloronaphthalene-2,6-*bis*-(sulfonyl chloride) [Beil. XI-216] (4), all with PCl_5, see indic. refs. cf. (6).]

[For study of oxidn. of C̄ with CrO_3/AcOH see (5).]

[C̄ with $ClSO_3H$ in CS_2 followed by conv. to salts yields a mixt. (1) derived from 2,3,6-trichloronaphthalenesulfonic acid-8 (corresp. sulfonyl chloride, m.p. 118° (1)), and from 2,3,6-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p 94° (1)).]

3:2455 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 256–257. (2) Armstrong, Wynne, *Chem. News* **61**, 275 (1890). (3) Armstrong, Wynne, *Chem. News* **61**, 92 (1890). (4) Armstrong, Wynne, *Chem. News* **62**, *163 (1890).* *(5) Claus, Schmidt, Ber.* **19**, *3177–3179 (1886).* (6) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 356, 377 (1921/22).

3:2460 5-CHLORO-2,4-DIMETHYLPHENOL
(6-Chloro-*m*-4-xylenol)



C_8H_9OCl Beil. VI - 488
VI_1-(242)
VI_2—

M.P. 90–91° (1) (2)

Ndls. from lgr. or aq. — Sol. hot aq. and most organic solvents. — Volatile with steam.

[For prepn. of C̄ *from 5-chloro-2,4-dimethylaniline* [Beil. XII_1-(480)] via diazotization and hydrolysis see (1); for formn. of C̄ from 2,4-dimethylquinol (*m*-xyloquinol) [Beil. VIII-22, $VIII_1$-(514)] by action of HCl (1) (2) in AcOH at 0° (1) (note that some of the isomeric 6-chloro-2,4-dimethylphenol (3:8784) is also formed) see indic. refs.]

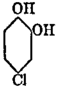
The nitration of C̄ has not been reported, and none of its mononitro- or dinitro-derivatives is known.

C̄ in alc. soln. with $FeCl_3$ gives a deep olive-green color becoming blue on dilution with aq. or reddish brown on htg. (1).

—— **5-Chloro-2,4-dimethylphenyl acetate:** unreported.
Ⓓ **5-Chloro-2,4-dimethylphenyl benzoate:** m.p. 84.5–85.5° (1). [From C̄ with benzoyl chloride + aq. NaOH (1).]
—— **5-Chloro-2,4-dimethylphenyl *p*-nitrobenzoate:** unreported.
—— **5-Chloro-2,4-dimethylphenyl *N*-phenylcarbamate:** unreported.

3:2460 (1) Bamberger, Reber, *Ber.* **46**, 793–803 (1913). (2) Bamberger, Reber, *Ber.* **40**, 2268 (1907).

3:2470 4-CHLOROCATECHOL (4-Chloropyrocatechol) $C_6H_5O_2Cl$ Beil. VI - 783, VI_1-(380), VI_2-(787)



M.P. 90–91° (1) (2)
88° (3)
80–81° (4)
(*See also text.*)

B.P. 139–139.5° at 10.5 mm. (1)
136–136.5° at 8.5 mm. (1)

Anhydrous C̄ exists in two forms melting at 90–91° and 59–61° (1); after fusion of the higher-melting form the resolidified C̄ melts 59–61° (1).

C̄ can be recrystd. from C_6H_6, $CHCl_3$ from which it separates in scaly lfts., or from CS_2 from which it separates in prisms. — C̄ cryst. from ord. ether as hemihydrate, C̄.½H_2O, which loses its aq. upon distn. in vac. (1). — C̄ is eas. sol. aq., alc., ether, AcOH, or acetone; spar. sol. lgr. (1).

[For prepn. of C̄ from catechol (1:1520) by action of $SOCl_2$ see (3) (5) (1) (4); for prepn. from 5-chloro-2-hydroxybenzaldehyde (3:2800) + alk. H_2O_2 see (6); for prepn. from *o*-benzoquinone [Beil. VII-600] by actn. of dry HCl in $CHCl_3$ see (7).]

C̄ with $FeCl_3$ gives scarab-green color, which on addn. of Na_2CO_3 becomes dark red, or with NaOAc turns blue (1).

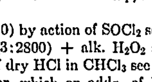
C̄ in AcOH treated with xanthydrol (1:5205) soon ppts. 4-chloro-5-xanthydrylcatechol, cryst. from C_6H_6, m.p. 224° (block) (8).

[For reaction with boric ac. see (2); for use in prepn. of dyestuffs see (9); for oxidn. with Ag_2O in abs. ether to 4-chlorobenzoquinone-1,2 see (1).]

Ⓓ 4-Chlorocatechol dibenzoate: from C̄ + BzCl in pyridine; ndls. (from ether), m.p. 96–97° (1).

3:2470 (1) Willstätter, Müller, *Ber.* **44**, 2182–2184 (1911). (2) Böeseken, Mijs, *Rec.* **44**, 758–760 (1925). (3) Frejka, Safranek, Zik, *Collection Czechoslov. Chem. Commun.* **9**, 245 (1937).
(4) Peratoner, *Gazz. chim. ital.* 28, I 222 (1898).
(6) Dakin, *Am. Chem. J.* **42**, 488 (1909). (7) J
(8) Fabre, *Ann. chim.* (9) **18**, 114–115 (1922).
1937; Cent. **1938**, *I 187.*

3:2475 1,1-DI-(*p*-CHLOROPHENYL)-ETHYLENE $C_{14}H_{10}Cl_2$ Beil. S.N. 480



M.P. 91° (1)
85–87° (2)

Colorless cryst. from MeOH contg. some C_6H_6 (1).

[For prepn. of C̄ from di-(*p*-chlorophenyl)-methyl-carbinol (itself prepared from 4,4′-dichlorobenzophenone (3:4270) with MeMgI) by dehydration see (1) (2).]

C̄ on cat. hydrogenation gives (62% yield (4)) 1,1-di-(*p*-chlorophenyl)ethane (3:0995), m.p. 54–55°.

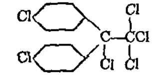
C̄ with PCl_5 in C_6H_6 stood 24 hrs. then poured into aq. gives (61% yield (1)) *β,β-bis*-(*p*-chlorophenyl)vinyl-phosphinic acid, $(Cl.C_6H_4.)_2C = CH.PO.(OH)_2$, cryst. from AcOH, m.p. 158–159° (1).

C̄ with O_3 in CCl_4 soln. in acetone/solid CO_2 cooling bath, subsequently decomposed with H_2O_2, gives (2) *p*-chlorobenzoic acid (3:4940), oxalic acid (1:0445), 4,4′-dichlorobenzophenone (3:4270), and a little 4,4′-dichlorobenzophenone peroxide, cryst from acetone, m p. 217.5–218.5° (2).

[For behavior of C̄ with C_6H_6 + $AlCl_3$ (3 moles) in reverse Friedel-Crafts reaction see (3)]

3:2475 (1) Bergmann, Bondi, *Ber.* **64**, 1470 (1931). (2) Marvel, Nichols, *J. Org. Chem.* **6**, 301 (1941). (3) Alexander, *Chem. Age* **36**, 50 (1937), *Cent.* **1937**, I 4085; not in *C.A.* (4) Grummitt, Buck, Becker, *J. Am. Chem. Soc.* **67**, 2265–2266 (1945).

3:2477 1,1,1,2-TETRACHLORO-2,2-*bis*-(*p*-CHLOROPHENYL)ETHANE $C_{14}H_8Cl_6$ **Beil. S.N. 479**



M.P. 91–92° (1)

Colorless cryst. from abs. alc.

[For prepn. of C̄ from 1,1,1-trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT") (3:3298) with Cl_2 in CCl_4 contg. a little PCl_3 (73% yield (1)), or from 1,1-dichloro-2,2-(*p*-chlorophenyl)ethylene (3:2438) with Cl_2 in $CHCl_3$ contg. a little PCl_3 (70% yield (1)), see indic. refs.

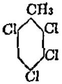
C̄ with Zn dust in abs. alc. refluxed 8 hrs loses 2 chlorine atoms giving (66% yield (1)) 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:2438).

Despite the presence in C̄ of one tertiary chlorine atom, C̄ does *not* (1) react with 5% alc. $AgNO_3$ at room temp.

C̄ with 5% aq. NaOH refluxed for 15 min is appreciably hydrolyzed, but with aq. alone similar treatment gives no appreciable reaction (1).

3:2477 (1) Grummitt, Buck, Jenkins, *J. Am. Chem. Soc.* **67**, 155–156 (1945).

3:2480 2,3,4,6-TETRACHLOROTOLUENE $C_7H_4Cl_4$ **Beil. V - 302**
V_1-(153)
V_2-(234)



M.P. 91.5–92° (1) (2)
92° (3)
91–92° (5)

Ndls. from alc., ether, or alc. + ether.

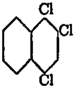
[For prepn of C̄ from 2,4,6-trichloro-3-aminotoluene [Beil. XII-873] (1) via diazotization and use of Cu_2Cl_2 reactn. (yield 92% (2)) (1) see indic. refs.; from toluene (1:7405) with Cl_2 in pres. of anhydrous $FeCl_3$ at 15–50° (90% yield) see (3) cf (5); for formn. of C̄ (together with other isomers) from 2,3,4-trichlorotoluene (3:0425) or 2,4,6-trichlorotoluene (3:0380) with Cl_2 in CCl_4 in pres of Al/Hg (2), or from 2,4,5-trichlorotoluene (3:2100) with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 as directed (4), see indic. refs]

C̄ (1 wt. pt) on nitration with a mixt of 3 wt pts. HNO_3 (D = 1.48) + 7.4 wt. pts. conc. H_2SO_4 (D = 1.84) at 105° for ½ hr. gives (4) 2,3,4,6-tetrachloro-5-nitrotoluene, cryst. from alc, m.p. 154° (4). — Note that the value of 131–134° reported previously (2) was undoubtedly (4) incorrect. — Note also that the m.p. of this nitration prod. is only

slightly lower than that (159°) for the corresp. prod. from 2,3,4,5-tetrachlorotoluene (3:2710).

3:2480 (1) Bures, Trpisovska, *Časopis Českoslov. Lékárnictva* **15**, 179–186 (1935); *Cent.* **1936**, I 1209; *C.A.* **30**, 1753 (1936). (2) Cohen, Dakin, *J. Chem. Soc.* **85**, 1280, 1282–1285 (1904). (3) Casella and Co., Ger. 282,567, April 7, 1915; *Cent.* **1915**, I 862. (4) Silberrad, *J. Chem. Soc.* **127**, 2682–2683 (1925). (5) Beilstein, Kuhlberg, *Ann.* **150**, 287–290 (1869).

3:2490 1,2,4-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V-544
V_1—
V_2—

M.P. 92° (1) (2)

Ndls. somewhat spar. sol. in alc. or AcOH.

[For prepn. of C̄ from 2,4-dichloronaphthylamine-1 [Beil. XII-1256] via diazotization and use of Cu_2Cl_2 reactn. see (1) (3); from 2,4-dichloronaphthol-1 (3:3250) by htg. with PCl_5 see (2); from 1,3-dichloronaphthalene (3:1310) with Cl_2 in $CHCl_3$ see (4).]

[C̄ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to Na salt as directed (1) yields sodium 1,2,4-trichloronaphthalenesulfonate-6 (corresp. sulfonyl chloride, m.p. 158° (1)).]

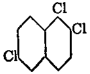
3:2490 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 251. (2) Cleve, *Ber.* **21**, 893 (1888). (3) Armstrong, Wynne, *Chem. News* **61**, 273 (1890). (4) Cleve, *Ber.* **23**, 954 (1890).

CHAPTER VII

DIVISION A. SOLIDS

(3:2500–3:2999)

3:2515 1,2,6-TRICHLORO-NAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V - 544
V_1—
V_2—

M.P. 92.5° (1)
92° (2) (8)
91° (3)
90° (4)

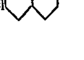
Ndls. from alc.; very eas. sol. $CHCl_3$.

[For prepn. of C̄ from 1-chloro-6-sulfonaphthylamine-2 [Beil. XIV-763] via diazotization and use of Cu_2Cl_2 reactn. see (2) (5); from 1,2-dichloronaphthalenesulfonyl chloride-6 [Beil. XI-183] (6), 2-chloro-1-nitronaphthalenesulfonyl chloride-6 [Beil. XI-188] (4), 2-chloronaphthalene-1,6-*bis*-(sulfonyl chloride) [Beil. XI-214] (3), or 1-chloro-6-bromo-naphthol-2 [Beil. VI-651] (7) by htg. with PCl_5 as directed see indic. refs.: for formn. of C̄ from 2,6-dichloronaphthalene (3:4040) with Cl_2 in $CHCl_3$ (9% yield) see (8).]

[C̄ treated with $ClSO_3H$ in CS_2 and prod. conv. to sodium salt yields (2) sodium 1,2,6-trichloronaphthalenesulfonate-4 (corresp. sulfonyl chloride, m.p. 184° (2))]

3:2515 (1) Armstrong, Wynne, *Chem. News* **71**, 255 (1895). (2) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 252. (3) Forsling, *Ber.* **21**, 3498 (1888). (4) Cleve, *Chem. Ztg.* **17**, 398 (1893). (5) Armstrong, Wynne, *Proc. Chem. Soc.* **1889**, 36, 49. (6) Armstrong, Wynne, *Chem. News* **59**, 189 (1889); **61**, 274 (1890). (7) Armstrong, Rossitter, *Chem. News* **63**, 137 (1891). (8) Wynne, *J. Chem. Soc.* **1946**, 61.

3:2545 3-CHLORONAPHTHOL-2



$C_{10}H_7OCl$ Beil. VI —
VI_1—
VI_2-(603)

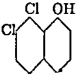
M.P. 93° (1)
92° (2)
90° (2)

Colorless ndls. from pet. ether. — Spar. sol. cold aq.; sol. boilg. aq., and readily sol. org. solvents. — Volatile with steam; can also be distilled without decompn. but b p. is not stated (2). [The identity of the product of m.p. 63–64 5° obtd. from supposed 3-chloronaphthyl-2 methyl ether by HI splitting (3) and regarded by its sponsors as C̄ is in doubt.] — Note that C̄ does *not* depress m.p. of β-naphthol (2).

[For prepn. of C̄ from 1,3-dichloronaphthol-2 (3:1990) with $Fe(OH)_2$ htd. under press. 8 hrs. at 120° (2) or htd. in alc. with Zn/Cu couple (1) see indic. refs.; from 3-chloronaphthalene-1,2-diazooxide with alk. $SnCl_2$ see (2); from 3-chloro-2-hydroxynaphthalenesulfonic acid-1 by htg. with 50% H_2SO_4 see (4).]

Michael, Clark, *J. prakt. Chem.* (2) **52**, 326–329 (1895). (19) Rosenmund, Zetsche, *Ber.* **51**, 583 (1918). (20) Michael, Schulthess, *J. prakt. Chem.* (2) **46**, 248–249 (1892).
(21) Kondakow, *J. Russ. Phys.-Chem. Soc.* **24**, 508 (1892). [illegible]
Chem. (2) **46**, 264–266 (1892). (23) Ostwald, *Z. physik. C* [illegible]
Ann. **219**, 346–349 (1883). (25) Michael, *J. prakt. Chem.* [illegible]
Schulthess, *J. prakt. Chem.* (2) **46**, 254–255 (1892). (27) M [illegible]
38, 1796–1797 (1916). (28) Autenrieth, *Ber.* **29**, 1665–16[illegible]
Am. Chem. Soc. **60**, 287 (1938). (30) Scheibler, Topouzac [illegible]
16 (1930).
(31) Nef, *Ann.* **276**, 234 (1893). (32) Autenrieth, *Ber.* **29**, 1646–1652 (1896). (33) Backer, Beute, *Rec. trav. chim.* **54**, 559–560; 622–624 (1935). (34) Koelsch, Hochmann, LeClaire, *J. Am. Chem. Soc.* **65**, 59 (1943). (35) Bergmann, Taubadel, Weiss, *Ber.* **64**, 1501 (1931). (36) Sudborough, Roberts, *J. Chem. Soc.* **87**, 1846 (1905). (37) Michael, Oechslin, *Ber.* **42**, 322 (1909).

3:2635 7,8-DICHLORONAPHTHOL-1 $C_{10}H_6OCl_2$ Beil. VI - 613
VI_1—
VI_2—



M.P. 95° (1) (2)

Ndls. from alc. (1) (2); much more sol. in lgr. than isomeric 6,7-dichloronaphthol-1 (3:4315) (3).

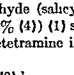
[For prepn. from β-(3,4-dichlorobenzal)propionic ac. [Beil. IX-614] by distn. see (1) (2) (3); C̄ is separated from the larger proportion of 6,7-dichloronaphthol-1 (3:4315) by its greater soly. in lgr. (3).]

C̄ in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a dark violet color which upon acidification turns bluish cherry-red (3). [Dif. from 6,7-dichloronaphthol-1 (3:4315) q.v.]

Ⓓ **7,8-Dichloro-1-naphthyl acetate:** cryst. from dil. alc., m.p. 87–88° (1) (2)

3:2635 (1) Armstrong, Wynne, *Chem. News* **71**, 253 (1895). (2) Armstrong, Wynne, *Proc. Chem. Soc.* **11**, 78–79 (1893); *Ber.* **29**, Referate 223–224 (1896). (3) Erdmann, Schwechten, *Ann.* **275**, 286 (1893).

3:2637 3,5-DICHLORO-2-HYDROXY-BENZALDEHYDE $C_7H_4O_2Cl_2$ Beil. VIII - 54
(3,5-Dichlorosalicylaldehyde) $VIII_1$—



M.P. **95–96°** (1)
95° (2) (3)
94–95° (4)

Pale yel. scales from AcOH; insol. aq., sol. in usual org. solvents.

[For prepn. of C̄ from *o*-hydroxybenzaldehyde (salicylaldehyde) (1:0205) in AcOH or $CHCl_3$ with Cl_2 (2moles) (yields: 90% (3), 70% (4)) (1) see indic. refs.; for formn. from 2,4-dichlorophenol (3:0560) with hexamethylenetetramine in glycerol + H_3BO_3 with H_2SO_4 as directed (7% yield) see (1).]

[For study of bactericidal props. of C̄ see (9).]

C̄ is sol. in dil. aq. alk or NH_4OH yielding yel. solns.; C̄ is stable toward dil. aq. acids or even hot conc. HCl but with conc. H_2SO_4 or HNO_3 dec. on warming (2).

[C̄ in dil. aq. NaOH oxidized with dil. (3%) H_2O_2 as directed yields (1) 3,5-dichloro-1,2-dihydroxybenzene (3,5-dichlorocatechol) (3:3525), pr. from cold aq, m.p. 83–84° (1)]

[C̄ with Ac_2O + NaOAc (Perkin condensation) yields (5) (6) 6,8-dichlorocoumarin,

cryst. from C_6H_6, m p. 160° (5), 157° (6) (this prod. on reduction with Na/Hg gives (6) γ-(3,5-dichloro-2-hydroxyphenyl)propionic acid (3,5-dichloromelilotic acid), m.p. 122° (6), on soln. in aq alk. and boilg. with HgO or $Hg(OAc)_2$ yields (7) 3,5-dichloro-2-hydroxycinnamic acid (3,5-dichloro-*o*-coumaric acid), cryst. from dil. alc., dec. 242° (7), or on oxidn. with $KMnO_4$ gives alm. quant. yield (5) of 3,5-dichlorosalicylic acid (3:4935), m p. 214° (5))] — [C̄ with ω-(phenylacetyl)acetophenone (1,4-diphenylbutanedione-1,3) in abs. alc. with a little piperidine 7–11 hrs. at 100° condenses giving (16% yield (8)) 6,8-dichloro-3-phenylcoumarin, colorless ndls. from AcOH, m p. 193–195° (8).]

[C̄ with EtMgBr yields corresp. ter. alc., viz., 3,5-dichloro-2-hydroxyphenyl-ethylcarbinol, which at 16 mm. press. loses aq. at 140° giving (80% yield (4)) 2,4-dichloro-6-propenylphenol, m p. 46–47° (4).]

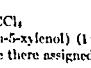
Ⓓ **3,5-Dichloro-2-hydroxybenzaldoxime** (3,5-dichlorosalicylaldoxime): colorless ndls. from alc./aq. (4:1) (3), m.p. 195–196° (4), 195° (2). [From C̄ + $NH_2OH.HCl$ in alc. on htg. 1 hr. and pouring into aq. (alm. quant. yield) (4).] [This oxime with Ac_2O on boilg. 3 hrs. gives alm. quant. yield (4) of 3,5-dichloro-2-acetoxybenzonitrile, colorless ndls from alc., m p. 78° (4)]

Ⓓ **3,5-Dichloro-2-hydroxybenzaldehyde phenylhydrazone**: pale yel. tbls. from alc., m p. 153° (1) [From C̄ in alc. with phenylhydrazine on shaking 10 min. (4).]

Ⓓ **3,5-Dichloro-2-hydroxybenzaldehyde semicarbazone**: alm. colorless ndls. from AcOH, m p 227° dec. (4) [From C̄ in AcOH with semicarbazide HCl in alm. quant. yield after ½ hr. boilg (4)]

3:2637 (1) Dakin, *Am. Chem J.* **42**, 488–489 (1909). (2) Duff, *J. Chem. Soc.* **1911**, 547–549. (3) Biltz, Stepf, *Ber.* **37**, 4027–4031 (1904). (4) Clausen, Tietze, *Ann.* **449**, 100 (1926). (5) Dey, Row, *J. Chem. Soc.* **125**, 560 (1924). (6) Chem. Werke Grenzach A G., Ger. 386,619, Dec. 13, 1923; *Cent.* **1924**, I 2033. (7) Sen, Chakravarti, *J. Indian Chem. Soc.* **7**, 249–250 (1930). (8) Lovett, Roberts, *J. Chem. Soc.* **1928**, 1977–1978. (9) Delauney, *J. pharm. chim.* (8) **25**, 254–266, 545–560 (1937), (8) **26**, 177–216 (1937), *Cent.* **1938**, I 2019.

3:2638 2,6-DICHLORO-3,5-DIMETHYL-PHENOL (2,6-Dichloro-*m*-5-xylenol)



$C_8H_8OCl_2$ Beil. S.N. 529

M.P. 95–96° (1)
(*See also text.*)

Cryst. from pet ether. — Eas. sol. $CHCl_3$, CCl_4

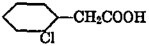
[For prepn. of C̄ from 3,5-dimethylphenol (*m*-5-xylenol) (1:1455) with SO_2Cl_2 (2 moles) in $CHCl_3$ see (1); note, however, that structure there assigned is 2,4-dichloro-3,5-dimethylphenol (3:2182) q.v]

The nitration of C̄ has not been reported, and the expected 4-nitro-2,6-dichloro-3,5-dimethylphenol is unknown.

—— **2,6-Dichloro-3,5-dimethylphenyl acetate**: unreported.
—— **2,6-Dichloro-3,5-dimethylphenyl benzoate**: unreported.

3:2638 (1) Lesser, Gad, *Ber.* **56**, 975 (1923).

3:2640 2-CHLOROPHENYLACETIC ACID $C_8H_7O_2Cl$ Beil. IX - 447
(o-Chloro-α-toluic acid) IX$_1$-(178)



M.P.	96°	(1)
	95–96°	(2)
	95°	(3) (4)
	94–95°	(2)
	94°	(6)
	92°	(5)

Colorless ndls. from aq [For study of ioniz. const. of C̄ see (1) (6) (9) (10) (13); for fate in animal body see (3); for studies of bacteriostatic props. see (11) (12).]

[For prepn. of C̄ from o-chlorobenzyl chloride (3:6400) via conversion to o-Cl.C_6H_4.-CH_2MgCl and subsequent carbonation with CO_2 see (2); from o-chlorophenylacetamide (see below) with nitrous acid see (3) (4) (6); from 2-phenyl-4-(2-chlorobenzal)oxazolone-5 (the azlactone from o-chlorobenzaldehyde + N-benzoylglycine + Ac_2O (5)) [Beil. XXVII$_1$-(298)] on boilg. with aq. NaOH and afterward treated with H_2O_2 see (5).]

[For reactns. of closely related o-Cl.C_6H_4.CH_2 COOMgCl with large excess of isopropyl MgCl or C_6H_5MgBr yielding o-chlorophenylmalonic acid, cryst. from alc., m.p. 139° (7), see (7) (8).]

[For condens. of C̄ with pyrene-3-aldehyde (14) or with N-ethylcarbazole-3-aldehyde (15) in prepn. of intermediates for dyes or pharmaceuticals see indic. refs.]

[C̄ with PCl_5 yields (3) 2-chlorophenylacetyl chloride, b.p. 119–121° at 12 mm., 118–120° at 10 mm.; this prod. with aminoacetic acid (glycine) in dil. aq. alk. gives (35% yield (3)) o-chlorophenylacetaminoacetic acid (o-chlorophenylaceturic acid), cryst. from hot aq., m.p. 134–135° (3).]

[C̄ converted to Pb salt, latter dried at 110° and distilled, yields (16) 2,2′-dichlorodibenzyl ketone, ndls. from alc., m.p. 102° (16) (oxime, m.p. 112° (16), semicarbazone, m.p. 149° (16)).] [For soly. of many other salts see (4).]

—— **Methyl 2-chlorophenylacetate:** oil, b.p. 125–128° at 23 mm. (4). [From C̄ in MeOH with HCl gas (4); also from o-Cl.C_6H_4.CH_2.MgCl with methyl chloroformate in ether (2); alkaline hydrolysis gives (2) C̄.]

—— **Ethyl 2-chlorophenylacetate:** oil, b.p. 134° at 23 mm. (4). [From C̄ in EtOH with HCl gas (4).]

Ⓓ **2-Chlorophenylacetamide:** lfts. from aq., m.p. 175° (4), 172–175° (3). [From 2-chlorophenylacetonitrile (o-chlorobenzyl cyanide) by partial hydrol. with H_2SO_4 (4) (3); actn. of HNO_2 yields C̄ (see above).]

Ⓓ **(2-Chlorophenylacet)anilide:** white ndls. from alc., m.p. 138.5° (4). [From C̄ + 1 mole aniline on htg. at 180–190° for ½ hr. (4).]

Ⓓ **(2-Chlorophenylacet)-m-chloroanilide:** white ndls. from dil. alc., m.p. 154° cor. (17). [From C̄ + m-chloraniline (1 mole) on htg. at 180–190° for 2 hrs. (17); also from o-chlorobenzyl m-chlorophenyl ketoxime by Beckmann rearr. with PCl_5 in ether (17).]

Ⓓ **(2-Chlorophenylacet)-p-toluidide:** white ndls. from dil. alc., m.p. 169.5° (4). [From C̄ on htg. with 1 mole p-toluidine as for the anilide (above) (4).]

Ⓓ **(2-Chlorophenylacet)phenylhydrazide:** white lfts. from C_6H_6, m.p. 175° (4). [From C̄ on htg. with 1 mole phenylhydrazine (as above) (4).]

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(7) Ivanov [illegible]

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3:2650 PARA-(β-CHLORO-n-BUTYRALDEHYDE)
(2,4,6-tris-(β-Chloro-n-propyl)-trioxane-1,3,5)

M.P. 96–97° (1)

Ndls. from dil. alc.; insol. aq. sol. [illegible]
[C̄ is readily chtd. by spontaneous [illegible]
C̄ on htg. with conc. H_2SO_4 [illegible] crotonaldehyde (1:01[illegible]
C̄ on oxidn. with CrO_3 yields [illegible] n-butyric acid (3:0[illegible]
C̄ on boiling with an aq. suspension of [illegible] acid.

3:2650 (1) Kekulé, *Ann.* 162, [illegible]

3:2662 1,1,1-TRICHLORO-2-METHYL-PROPANOL-2
(β,β,β-Trichloro-[illegible] alcohol; acetone chloroform; "Chloretone"; "Chlorbutol")

M.P. 97°	[illegible]	[illegible]	
96–97°	[illegible]		[illegible]
96.2°	[illegible]		
96°	[illegible]	[illegible]	

Colorless cryst. [illegible] when placed on clean [illegible]
C̄ is spar. sol. cold aq. [illegible] (7) (8)).—C̄ is [illegible]
C̄ is very easily [illegible] (19)).—From [illegible] (5), 8[illegible] a benzylthiuronium [illegible] a solid soln. of [illegible]

[illegible] ne
[illegible] iso-
[illegible] yric
[illegible] with
[illegible] ne +
[illegible] odor of
[illegible] n. gives
[illegible] −152° at
[illegible]) refluxed
[illegible] flux (37%
[illegible] OH at 100°
[illegible] boilg. with
[illegible] C̄ (43))
[illegible] , m.p. 34–35°
[illegible] rs.) (44) (45),
[illegible] that this ester
[illegible] aliphatic acids,
[illegible] richloro-*ter*-butyl
[illegible] (46) (47). [From
[illegible] ° (46) (47). [From
[illegible] m β,β,β-trichloro-*ter*-
[illegible] low 50° (46) (47).]
[illegible] m.p. 145° (46) (47).
[illegible] p. 102° (48) (49). [From
[illegible] onversion of the presumably
[illegible] toluene to β,β,β-trichloro-*ter*-
[illegible] he latter in the C_6H_6/toluene
[illegible] at earlier attempts (26) to obtain
[illegible] xplosions (cf. alkali metals with
[illegible] ndls. from C_6H_6, m.p. 118° (48).
[illegible] dine was used in place of NH_3 in last
[illegible] bamate: unreported.

removes the aq. and yields (5) anhydrous C̄ (for conv. of the " hemihydrate " to anhydrous C̄ by use of CaO, $CaCl_2$, $MgCl_2$ see (12)); note, however, that anhydrous C̄ on stdg. in air is converted to the " hemihydrate " in less than 30 min. (11). — C̄ readily sublimes even at room temp. and by repeated sublimation yields (18) anhydrous form.

C̄ has hypnotic, sedative, local anesthetic, and antiseptic characteristics and finds extensive use in medicine and in preservation of biological solns.; it has been used in treatment of nausea and seasickness, e g., German " Nautissan " or (together with caffeine) as the British " Motherhill's Seasick Remedy " (10).

C̄ is also employed as a modifier for cellulose acetate (13) (14) (15) (16) or cellulose ethers (17).

[For detn. of C̄ by complete hydrolysis with hot MeOH/KOH and subsequent detn. of chlorine by either volumetric or gravimetric methods see (3) (19).]

[For prepn. of C̄ from acetone (1:5400) + $CHCl_3$ (3:5050) by addn. of dry powdered KOH (0 5 mole) below 0° (5) or 2–3° (4) or KOH in alc. as directed (11) (yields: 25% (11), 23% (5)) (2) (4) see indic. refs.; note that use of NaOH lowers the yield (5) and that $Ca(OH)_2$ (11), $Zn(OH)_2$ (5), or $Al(OH)_3$ (5) yields no C̄; note also that the crude prod. contains some diacetone alcohol (1:6423) which is best removed by treatment with aq. (11) since otherwise it appears to form with C̄ a const.-boilg. mixt.

[For prepn. of C̄ from trichloroacetyl chloride (3:5420) with MeMgI in ether (4) or from ethyl trichloroacetate (3:5950) with MeMgBr in ether (20) see indic. refs.]

[C̄ with granulated Zn + conc. HCl (in pres. of a little ether) is reduced (21) to *ter*-butyl alc. (1:6140), m.p. 25°, but C̄ in 70% alc. warmed with Zn dust for 5 hrs. gives (4% yield (22)) 1,1-dichloro-2-methylpropene-1 (3:5300) + 1-chloro-2-methylpropene-1 (3:7120) + isobutylene (23). — C̄ with granulated Zn in boilg. AcOH yields (21) *ter*-butyl acetate (1:3057).]

[C̄ with Na/Hg in moist ether (21), or with aq. in s.t. at 180° for 3 hrs. (24), or C̄ with aq. alc. KOH (25) undergoes hydrol. of its $—CCl_3$ group yielding α-hydroxy-isobutyric acid (1:0431), m.p. 79°.]

Anhydrous C̄ in dry ether poured onto a lower layer of colorless fuchsin-aldehyde reagt. (Schiff's soln.) gives a purple color (26), but this behavior is not shown by the " hemihydrate." — C̄ also reduces $NH_4OH/AgNO_3$ soln. slowly in the cold (2).

[C̄ with cold 10% aq. KOH is claimed (27) cf. (29) to yield traces of α-chloroisobutyric acid (3:0235) or carbon monoxide + acetone (28), while C̄ with solid KOH gives (27) methacrylic acid [Beil. II-421, II_2-(398)], and C̄ in MeOH with alk. or tertiary org. bases, or mineral acids, yields (29) methyl methacrylate [Beil. II_2-(398)].]

C̄ with conc. H_2SO_4 (10 wt. pts.) evolves CO + CO_2 + HCl (25) (26); the CO presumably results from the usual action of H_2SO_4 on some α-hydroxy-isobutyric acid (1:0431) first formed by hydrolysis; for the other reactions see (25).

[C̄ with PCl_5 at 100° is claimed (30) (31) (21) to yield both *bis*-(β,β,β-trichloro-*ter*-butyl) ether [Beil. I-383, I_1-(193)], b.p. 156° (30), and 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m p and b p. both at 167° (30), but later workers (26) could obtain no reaction at all between C̄ and PCl_5. — C̄ with PBr_5 at 60° (not above because of dissociation of PBr_5) gives (32) cf. (21) 2,3-dibromo-1,1,1-trichloro-2-methylpropane, b p. 243° (32).]

C̄ with P_2O_5 in dimethylaniline (1) or quinoline (50) htd. at 200° under ord. press. gives (yield: 30–43% (50), 15% (33)) 1,1,1-trichloro-2-methylpropene-2 (3:5605), b.p. 132°, + 57% yield of its synionic isomer 1,1,3-trichloro-2-methylpropene-1 (3:5025), b.p. 45–46°, accompanied by some α-chloroisobutyric acid (3:0235) cf. (50).

[Various reactions of C̄ have been employed in prepn. of pharmaceutical prods.: C̄ with adipic anhydride (see text of 1:0775) at 160–180° for 8 hrs. (35), or C̄ with adipic acid (1:0775) + $SOCl_2$ grad. htd. to 150–160° (36), gives β,β,β-trichloro-*ter*-butyl hydrogen

adipate, cryst. from pet. ether, m p. 70° (35). — $\bar{C}$ with 5-ethyl-5-phenyl-barbituric acid ("Luminal") does *not* (37) show evidence of molecular cpd. formn. but forms a eutectic, m.p. 70.4°, *contg.* 90% $\bar{C}$. — $\bar{C}$ with 2,3-dimethyl-1-phenylpyrazolone-5 ("Antipyrine") does *not* (38) form a molecular cpd. but gives a eutectic contg. 60 mole % $\bar{C}$. — $\bar{C}$ with 2,3-dimethyl-4-dimethylamino-1-phenylpyrazolone-5 ("Pyramidone") gives (39) a molecular cpd., m p. 61–63°. — $\bar{C}$ with chloral (3:5210) or chloral hydrate (3:1270) gives (40) a molecular cpd, m.p. 65°. — See also above (paragraph 4) and below (under Ⓓ's).]

[For reactn. of $\bar{C}$ + $AlCl_3$ (in Friedel-Crafts sense) with benzene, toluene, and *p*-xylene see (31); for reactn of $\bar{C}$ with ethyl sodio-acetoacetate see (25)]

[$\bar{C}$ with aniline in alc. KOH gives according to conditions (41) either β(or α)-anilinoisobutyranilide [Beil. XII-558], cryst. from alc, m.p. 155–157° (41), or β-anilinoisobutyric acid [Beil. XII-497], cryst. from alc., m p 185° (41). — For study of reactions of $\bar{C}$ with *p*-ethoxyaniline (*p*-phenetidine) + alc. KOH see (42); of $\bar{C}$ with *o*-phenylenediamine + alc. KOH see (41)]

Ⓟ **Carbylamine test:** $\bar{C}$ with aniline + aq. alk. on warming gives characteristic odor of phenyl isocyanide (phenyl carbylamine).

Ⓟ **Iodoform reaction:** $\bar{C}$ in aq. soln. (1/200) treated with aq NaOH + I_2/KI soln gives yel. ppt. of iodoform (m p. 119°) with its characteristic odor.

—— **β,β,β-Trichloro-*ter*-butyl acetate:** oil, b.p. 191° (21), 190–191° (4), 151–152° at 237 mm (43). [From $\bar{C}$ (1 pt.) with Ac_2O (2 pts.) + anhyd. NaOAc (1 pt.) refluxed 2 hrs (85% *yield* (43)), *or from* $\bar{C}$ (1 *mole*) *with AcCl* (1 *mole*) *under reflux* (37% yield (21)).] — [Note that this ester, although unaffected by 10% aq. NaOH at 100° for 20 min. (dif. from $\bar{C}$ which is hydrolyzed), is rapidly saponified by boilg. with 3–4 vols. conc. HNO_3 for a few minutes, and upon dilution with aq. ppts. $\bar{C}$ (43)]

Ⓓ **β,β,β-Trichloro-*ter*-butyl benzoate:** cryst. from alc. upon addn. of aq, m.p. 34–35° (44) (45). [From $\bar{C}$ with BzCl at 100° until evoln. of HCl stops (6 hrs.) (44) (45), or from $\bar{C}$ + benzoic acid (1:0715) in pres. of $ZnCl_2$ (45)] — [Note that this ester on boilg. with conc. HNO_3 is *not* hydrolyzed (dif. from esters of $\bar{C}$ with aliphatic acids, e.g, acetate (above)), but nitrated (46) yielding mainly β,β,β-trichloro-*ter*-butyl *m*-nitrobenzoate (see below).]

Ⓓ **β,β,β-Trichloro-*ter*-butyl *o*-nitrobenzoate:** pl. from alc., m.p. 91° (46) (47) [From $\bar{C}$ with *o*-nitrobenzoyl chloride on warming (46) (47).]

Ⓓ **β,β,β-Trichloro-*ter*-butyl *m*-nitrobenzoate:** pl. from alc., m.p. 87° (46) (47). [From $\bar{C}$ with *m*-nitrobenzoyl chloride on warming (46) (47), or from β,β,β-trichloro-*ter*-butyl benzoate (above) by nitration with excess conc. HNO_3 below 50° (46) (47)]

Ⓓ **β,β,β-Trichloro-*ter*-butyl *p*-nitrobenzoate:** ndls. from alc., m.p. 145° (46) (47). [From $\bar{C}$ with *p*-nitrobenzoyl chloride on warming (46) (47).]

Ⓓ **β,β,β-Trichloro-*ter*-butyl 3,5-dinitrobenzoate:** unreported.

—— **β,β,β-Trichloro-*ter*-butyl carbamate:** pl. from C_6H_6, m.p. 102° (48) (49). [From $\bar{C}$ with Na in C_6H_6 at room temp. for 4 hrs., followed by conversion of the presumably resultant metal alcoholate with phosgene (3:5000) in toluene to β,β,β-trichloro-*ter*-butyl chloroformate (not isolated), and reaction of the latter in the C_6H_6/toluene soln. with dry NH_3 gas (55% yield (48)) (49); note that earlier attempts (26) to obtain a metal alcoholate in toluene had led to serious explosions (cf. alkali metals with $CHCl_3$) (3:5050).]

—— **β,β,β-Trichloro-*ter*-butyl *N*-phenylcarbamate:** ndls. from C_6H_6, m.p. 118° (48). [From $\bar{C}$ as in the preceding case except that aniline was used in place of NH_3 in last step; yield is poor (48)]

—— **β,β,β-Trichloro-*ter*-butyl *N*-(α-naphthyl)carbamate:** unreported.

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... 3322
... *Soc.*
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... (47)
... (48)
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3:2075 1,3-DICHLORO-2,2-*bis*(CHLOROMETHYL)PROPANE (Pentaerythrityl tetrachloride)

$$\begin{array}{c} CH_2Cl \\ | \\ ClCH_2-C-CH_2Cl \\ | \\ CH_2Cl \end{array}$$

$C_5H_8Cl_4$ Beil. I - 141
I_1—
I_2-(104)

M.P. 97° (1) (2) (3) (5) **B.P. 110° at 12 mm.** (1) (2)
100° at 12 mm. (5)

Colorless cryst. with camphoraceous odor. — Sublimes; cas. volatile with steam. — Insol. aq.

[For prepn. of C̄ from pentaerythritol (1:5850) with 4 moles $SOCl_2$ + 4 moles pyridine (3) cf. (4) (5) or with conc. HCl in s.t. at 150° followed by PCl_3 (2) or on htg. the trichlorohydrin (1) with PCl_5 at 150° see indic. refs. (1).] [Note that pentaerythritol (1:5850) on htg. in s.t. with conc. HCl at 120–180° gives (1) a mixt. of mono-, di-, and trichloro-

hydrins: the monochlorohydrin, $(HOCH_2)_3C.CH_2Cl$, m.p. 141°, b.p. 190° at 12 mm., is sol. in aq.; the dichlorohydrin, $(HOCH_2)_2C(CH_2Cl)_2$, m.p. 95°, b.p. 160° at 12 mm., is sol. in aq. + C_6H_6; the trichlorohydrin, $HOCH_2$—C≡$(CH_2Cl)_3$, m.p. 80°, b.p. 136° at 12 mm., is sol. in C_6H_6 + pet. ether (1); note also that pure dichlorohydrin has recently (6) been reported as m p. 79–80°.]

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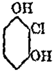
3:2690 2-CHLORORESORCINOL  $C_6H_5O_2Cl$ Beil. S.N. 554

M.P. 97–98° u.c. (1)
94° (2)

[*See also 4-chlororesorcinol* (3:3100) *and 5-chlororesorcinol* (3:3530).]

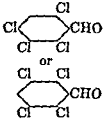
Colorless cryst. purified by sublimation.

[For prepn. of C̄ from 2,4-dihydroxy-5-nitrobenzoic acid (5-nitro-β-resorcylic acid) [Beil. X-382, X_1-(179)] via chlorination with SO_2Cl_2 in AcOH to 3-chloro-2,4-hydroxy-5-nitrobenzoic acid, reduction of the latter with $SnCl_2$/HCl in AcOH to 3-chloro-2,4-dihydroxy-5-aminobenzoic acid, with final removal of the amino group by diazotization and use of alk. $SnCl_2$, see (1).]

[C̄ is formed in small amt. together with 4-chlororesorcinol (3:3100) from resorcinol (1:1530) by actn. of *N,N*-dichlorourea (2).]

[Note that attempts (3) cf. (1) to prepare C̄ from 2-aminoresorcinol [Beil. XIII-782] by diazotization and use of Sandmeyer reactn. have failed because the actn. of nitrous acid yields 4-nitroso-2-diazoresorcinol.]

[The prod , m.p. 89°, b.p. 255–256°, obtained (4) from resorcinol (1:1530) with SO_2Cl_2 in ether may have contained C̄.]

3:2700 2,3,4,6-(or 2,3,5,6-) TETRACHLOROBENZALDEHYDE  $C_7H_2OCl_4$ Beil. VII — VII_1-(134)

M.P. 97–98° (1)

Ndls. from pet. ether. — Eas. sol. ether, C_6H_6, or $CHCl_3$; spar. sol. alc. or pet. ether; insol. aq

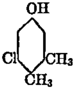
[For prepn. of C̄ from 2,3,4,6-tetrachlorobenzal (di)chloride (3:6980) by hydrolysis with conc. H_2SO_4 at 96° see (1)]

$\bar{C}$ with $NaHSO_3$ forms the corresp. addn. cpd.; spar. sol. cold aq. (1); for use in sepn. of $\bar{C}$ from 2,3,4,5-tetrachlorobenzaldehyde (3:3140) see (2).

[For use of $\bar{C}$ in prepn. of dyes of the triphenylmethane series see (3).]

3:2700 (1) Cassella and Co., Ger. 290,209, Feb. 8, 1916; *Cent.* **1916**, I 396–397; not in *C.A.* (2) Chem. Fabrik Griesheim Elektron, Brit. 251,511, May 27, 1926; *Cent.* **1926**, II 2355; *C.A.* **21**, 1361 (1927): French 603,650, April 20, 1926; *Cent.* **1926**, II 2355; not in *C.A.* (3) Cassella and Co., Ger. 302,138, Nov. 28, 1917; *Cent.* **1918**, I 250; not in *C.A.*

3:2705 5-CHLORO-3,4-DIMETHYLPHENOL (6-Chloro-*o*-4-xylenol) C_8H_9OCl Beil. VI — VI_1— VI_2-(456)



M.P. 98° (1) (2)

Ndls. from lt. pet. — Volatile with steam.

[For prepn. of $\bar{C}$ from 5-chloro-3,4-dimethylaniline (6-chloro-*o*-4-xylidine) (1) via diazotization and hydrolysis (yield not stated) see (1); from 6-amino-5-chloro-3,4-dimethylphenol (6-chloro-5-amino-*o*-4-xylenol) (2) via diazotization and elimination of original amino group using Cu_2Cl_2 reaction (unusual) (yield not stated) see (2).]

$\bar{C}$ with Cl_2 in $CHCl_3$ gives (1) 2,5,6-trichloro-3,4-dimethylphenol (3:4747), m.p. 182.5°.

The nitration of $\bar{C}$ has not been reported, and neither of the two possible mononitro derivs. nor the corresp. dinitro deriv. is known.

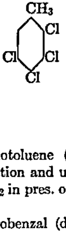
$\bar{C}$ in alk. soln. couples with benzenediazonium chloride giving (2) the corresp. azo cpd., red ndls. from alc., m.p. 143° (2).

—— **5-Chloro-3,4-dimethylphenyl acetate:** unreported.

Ⓓ **5-Chloro-3,4-dimethylphenyl benzoate:** m.p. 42° (1).

3:2705 (1) Hinkel, *J. Chem. Soc.* **125**, 1853 (1924). (2) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 2532.

3:2710 2,3,4,5-TETRACHLOROTOLUENE $C_7H_4Cl_4$ Beil. V - 302 V_1— V_2-(233)



M.P. 98.1° cor. (1)
97–98° (2) (3)

Ndls. from MeOH.

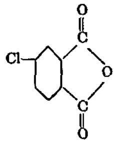
[For prepn. of $\bar{C}$ from 3,4,5-trichloro-2-aminotoluene (3) or from 2,4,5-trichloro-3-aminotoluene [Beil. XII-872] (2) (3) via diazotization and use of Cu_2Cl_2 reactn. see indic. refs.; from 3,4,5-trichlorotoluene (3:0580) with Cl_2 in pres. of Al/Hg (2) (3) or with SO_2Cl_2 + $AlCl_3$ + S (35% yield (1)) see indic. refs.]

[$\bar{C}$ at b.p. with Cl_2 yields (4) 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397).]

$\bar{C}$ on nitration with 6 pts. of a mixt. of 2 pts. HNO_3 (D = 1.48) + 4 pts. H_2SO_4 (D = 1.84) at 105° for ½ hr. (1) yields 2,3,4,5-tetrachloro-6-nitrotoluene, m.p. 159.6° cor. (1), 159° (3).

3:2710 (1) Silberrad, *J. Chem. Soc.* **127**, 2682–2 ... *J. Chem. Soc.*
85, 1280, 1285 (1904). (3) Cohen, Dakin, *J.*
Fabrik Griesheim-Elektron, Brit. 251,511, May
1926, II 2355.

3:2725 4-CHLOROPHTHALIC ANHYDRIDE



$C_8H_3O_3Cl$ Beil. XVII - 483
XVII$_1$-(253)

M.P.	98.5°	(1)	B.P. 294.5° cor.	at 720 mm.	(6)
	98°	(2) (3) (4) (13)	297°		(3)
	97°	(5)	291–295°		(3)
	96–97°	(6)	286–290°		(4)
	95°	(7) (8)	287°	at 760 mm.	(2)
	90–94°	(3)			

[*See also 4-chlorophthalic acid* (3:4390).]

Cryst. from CCl_4 (5) (4), from Ac_2O (2), from ether, or from alc. (For crystallographic consts. see (2)) — Eas. sol. alc., ether, $CHCl_3$; less sol. CS_2; spar. sol. lgr.

[For use of $\bar{C}$ with glycerol or ethylene glycol in prepn. of glyptal type resins see (26).]

[For prepn. of $\bar{C}$ from 4-chlorophthalic acid (3:4390) by htg. or sublimation (6) (7) (8) (1) (9) or by htg with AcCl (2) see indic. refs; from $NaH\bar{A}$ with conc. H_2SO_4 at 100° see (10); from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe or Fe salts at 160–260° see (11) (note that crude $\bar{C}$ obtd. by chlorination methods or from 4-chlorophthalic acid obtd. by chlorination methods may cont. dichlorophthalic anhydrides from which $\bar{C}$ is separable by its greater soly. in toluene (4)); from 4-nitrophthalic anhydride [Beil. XVII-486, XVII$_1$-(256)] with Cl_2 at 240° see (12)]

[$\bar{C}$ with Cl_2 in fumg H_2SO_4 in pres. of I_2 gives (13) mixt. contg much 3,4-dichlorophthalic anhydride (3:3695), m.p. 120–121°, b.p. 329°, and little 4,5-dichlorophthalic anhydride (3:4830), m p. 187°.]

[$\bar{C}$ with $SOCl_2 + ZnCl_2$ in s.t. at 240° yields (27) 4-chlorophthalyl (di)chloride [Beil. IX-817], b.p. 275–276° (6).]

[$\bar{C}$ in MeOH satd. with dry HCl yields (6) dimethyl 4-chlorophthalate, ndls. from lgr., m.p. 38° (5), m.p. 37° (6), b p. 186–187° at 32 mm. (5); $\bar{C}$ in EtOH similarly gives (6) diethyl 4-chlorophthalate, b p 173–174° at 16 mm. (14), 300–305° (6)]

$\bar{C}$ fused and treated with dry NH_3 gas (6) or $\bar{C}$ htd with urea (28) yields 4-chlorophthalimide [Beil XXI-503, XXI$_1$-(391)], m p 210–211° (6) (3). [Ring opening of this prod. with NaOCl yields (9) 3 pts. 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV$_1$-(518)], m p. 235–236° (9), and 1 pt. 5-chloro-2-aminobenzoic acid as "anhydride," m.p 178–179° (9)] [For use of 4-chlorophthalimide in prepn. of pigments of phthalocyanine type see (28).]

[$\bar{C}$ fused with aminoacetonitrile hydrochloride or sulfate yields (15) 4-chlorophthalimidoacetamide, ndls. from hot aq., m p. 241° (15); $\bar{C}$ htd with methyleneaminoacetonitrile until evoln of CH_2O ceases yields (15) 4-chlorophthalimidoacetonitrile, ndls. from dil. AcOH, m p 146.5° (15); $\bar{C}$ htd. with glycine yields (15) 4-chlorophthalimidoacetic acid, yel. pl. from hot aq or dil alc., m p. 205° (15)]

[$\bar{C}$ with 2 moles phenol htd with $ZnCl_2$ at 115–130° for 48 hrs. as directed (2) gives 70% yield phenol (di)chlorophthalein, m p 214–233°, and prob. a mixt. of isomers; $\bar{C}$ with resorcinol htd with trace conc. H_2SO_4 yields (6) a prod. behaving as dichlorofluorescein. — Note, however, that $\bar{C}$ with hydroquinone (1:1590) + $AlCl_3$ + NaCl htd. at 200–220°

(4) or $\bar{C}$ with *p*-chlorophenol (3:0475) + fumg. H_2SO_4 + H_3BO_3 htd. 20 hrs. at 175–195° gives (95% yield (4)) 6-chloro-1,4-dihydroxyanthraquinone (6-chloroquinizarin), tbls. from toluene, m.p. 188° (diacetate, m.p. 213°, dimethyl ether, m.p. 168.5° (4)).]

[$\bar{C}$ with C_6H_6 + $AlCl_3$ yields (6) (3) 4-chloro-2-(benzoyl)benzoic acid [Beil. X-750, X_1-(356)], cryst. from xylene, m.p. 180.5° (3), from C_6H_6, m.p. 170° (6) (this on ring closure with conc. H_2SO_4 at 160–170° for 10 min. gives 2-chloroanthraquinone (3:4922), m.p 204° (3). — $\bar{C}$ with chlorobenzene (3:7903) + $AlCl_3$ yields (3) (17) 4-chloro-2-(*p*-chlorobenzoyl)benzoic acid [Beil. X_1-(357)], cryst. from xylene, m.p. 195.5° (3) (this on ring closure as above gives (3) 2,6-dichloroanthraquinone [Beil. VII-788, VII_1-(413)], m.p. 278° (3)). — For similar condensations of $\bar{C}$ + $AlCl_3$ with *p*-dichlorobenzene see (3), with bromobenzene see (18), with naphthalene see (25) (19), with toluene see (19) (20), with perylene see (21) (22), with 2,2′-dinaphthyl see (23).]

[For use of $\bar{C}$ in prepn. of pigments of the phthalocyanine type see (24) (28).]

$\bar{C}$ on warming with aq. readily hydrolyzes; $\bar{C}$ on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidification yields 4-chlorophthalic acid (3:4390) q.v.

3:2725 (1) Miersch, *Ber.* **25**, 2116 (1892). (2) Blicke, Smith, *J. Am. Chem. Soc.* **51**, 1871–1872, 1874 (1929). (3) Egerer, Meyer, *Monatsh.* **34**, 81–83, 86, 90 (1913). (4) Waldmann, *J. prakt. Chem.* (2) **126**, 254–255 (1930). (5) Ayling, *J. Chem. Soc.* **1929**, 255. (6) Rée, *Ann.* **233**, 236–240 (1886). (7) Alén, *Bull. soc. chim.* (2) **36**, 434 (1881). (8) Claus, Dehne, *Ber.* **15**, 320 (1882). (9) Moore, Marrack, Proud, *J. Chem. Soc.* **119**, 1788–1789 (1921). (10) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 347,666, May 28, 1931; *Cent.* **1931**, II 1195.

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* **1936**, I 2830; *C.A.* **30**, 1394 (1936). (12) Imperial Chem. Ind., Ltd., Shaw, Thomas, Brit. 357,165, Oct. 15, 1931; *Cent.* **1931**, II 3663. (13) Villiger, *Ber.* **42**, 3594 (1909). (14) von Braun, Larbig, Kredel, *Ber.* **56**, 2338 (1923). (15) Stephen, *J. Chem. Soc.* **1931**, 871–873. (16) Scottish Dyes, Ltd., Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; *Cent.* **1932**, I 2095; *C.A.* **25**, 2859 (1931). (17) Müller (to I.G.), Ger. 495,447, April 7, 1930; *Cent.* **1931**, I 1675. (18) Waldmann, *J. prakt. Chem.* (2) **126**, 74–75 (1930). (19) B.A.S.F., Ger. 234,917, May 26, 1911; *Cent.* **1911**, II 114. (20) B.A.S.F., Ger. 211,927, July 14, 1909; *Cent.* **1909**, II 396.

(21) Zinke, Gorbach, Shimka, *Monatsh.* **48**, 593–598 (1927). (22) Nawiasky, Grosskinsky (to I.G.), Ger. 642,650, March 11, 1937; *Cent.* **1937**, I 5057. (23) Neresheimer, Kacer (to I.G.), Ger. 565,425, Nov. 30, 1932; *Cent.* **1933**, I 1358. (24) Imperial Chem. Ind., Ltd., French 808,845, Feb. 16, 1937; Brit. 464,126, April 12, 1937; *Cent.* **1937**, II 3820; *C.A.* **31**, 6255 (1937). (25) Schwenk, Waldmann, *J. prakt. Chem.* (2) **128**, 320–326 (1930). (26) Kogan, Ponomarenko, *Org. Chem. Ind.* (*U.S.S.R.*) **7**, 382–385 (1940); *C.A.* **35**, 4118 (1941). (17) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; *Cent.* **1934**, II 333. (28) Imperial Chem. Ind., Ltd., Heilbron, Irving, Linstead, Thorpe, Brit. 410,814, June 21, 1934; French 763,993, May 12, 1934; *Cent.* **1935**, I 1305.

3:2760 α-CHLOROCROTONIC ACID (*trans*-2-Chlorobuten-2-oic acid)

$C_4H_5O_2Cl$ Beil. II - 414, II_1-(189), II_2-(395)

M.P.	**99.5–100°**	(1) (15)	**B.P. 212°** (10) (11)
	99–100°	(2) (3)	**111–112° at 14 mm.** (11)
	99–99.5°	(6)	
	99.5°	(4)	
	99.2°	(5) (26)	
	99°	(7) (12) (27)	
	98.5–99°	(8) (11)	
	97–98°	(17)	
	97.5°	(9) (20)	
	96°	(10)	

[*See also α-chloroisocrotonic acid* (3:1615).]

Ndls. from aq. (4) (20) or pet. eth. (8). — $\bar{C}$ is sol. in 47.1 pts. aq. at 19° (13); 100 pts. satd. aq. soln. at 12.5° cont. 1.97 pts. $\bar{C}$ (9). — $\bar{C}$ is less (9) (5) volatile with steam than the isomeric α-chloroisocrotonic acid (3:1615). — Eas. sol. alc. or ether (10). — Readily sublimes (10). — Note that the m.p. of mixts. of $\bar{C}$ with β-chlorocrotonic acid (3:2625) is depressed far below either (4).

[For thermal anal. of system $\bar{C}$ + 2,6-dimethylpyrone see (12); with conc. H_2SO_4 see (14).]

Preparation. For prepn. of $\bar{C}$ from α,α,β-trichloro-n-butyric acid (3:1280) [itself readily obtd. from α,α,β-trichloro-n-butyraldehyde (butylchloral) (3:5910) by oxidn. with HNO_3] by *removal of two halogen atoms with Zn dust + aq. (83% yield on initial butylchloral hydrate (3))* (10), or with Zn + HCl (15), see indic refs.; from the higher-melting form of α,β-dichloro-n-butyric acid ("isocrotonic acid dichloride") (3:1903) by splitting out HCl with alc. KOH see (17) (18); from the lower-melting form of α,β-dichloro-n-butyric acid ("crotonic acid dichloride") (3:1375) by splitting out HCl with excess aq. NaOH (5) (18) or with pyridine at 100° for 3 hrs. (4) or with 1% Am_3N refluxed at 160–180° for 16 hrs. (85% yield (28)) (note, however, that with NaOH the yield is low and much of the isomeric α-chloroisocrotonic acid (3:1615) is formed); from α-chloro-β-hydroxy-n-butyric acid [Beil. III-309, 310] by elimination of H_2O with warm 80% H_2SO_4 see (17).]

[For prepn. of $\bar{C}$ from α,α,β-trichloro-n-butyraldehyde (butylchloral) (3:5910) by simultaneous oxidn. and elimination of HCl with aq. $K_4Fe(CN)_6$ (yield 44.3% (3)) (19) see indic. refs.]

[For formn. of $\bar{C}$ from crotonic acid (1:0425) by actn. of Cl_2 and distillation of product see (20); from α-chloroisocrotonic acid (3:1615) by htg. in s.t. at 150–160° for 12 hrs. (21), with pyridine HCl in pyridine 7 days at room temp (4), or to small extent even on steam distn. (22) see indic. refs.; from the methyl, ethyl, or n-propyl esters of α-chloro-α-vinylacetic acid or from α-chloro-α-vinylacetonitrile (or amide) on hydrolysis with alkali (note shift of double bond from β,γ to α,β position) see (11); from ethyl α-chlorocrotonate (3:8523) by hydrolysis with conc. HCl see (23).]

Chemical behavior. [$\bar{C}$ on reduction with Na/Hg is dehalogenated yielding (10) crotonic acid (1:0425), m.p. 72°; note, however, that $\bar{C}$ does not readily absorb H_2 even in pres. of Pt black (11).]

$\bar{C}$ with Cl_2 in CS_2 adds 1 mole halogen yielding (24) α,α,β-trichloro-n-butyric acid (3:1280), m.p. 59.5–60°. — $\bar{C}$ adds Br_2 readily (15) yielding (10) α,β-dibromo-α-chloro-n-butyric acid [Beil. II-286], m.p. 92° (10).

$\bar{C}$ with fumg. HCl in s.t. at 100° for 5 hrs. adds 1 HCl to double bond yielding (17) (18) the higher-melting α,β-dichloro-n-butyric acid (3:1903), m.p. 78°.

$\bar{C}$ behaves as a monobasic acid; dissociation const. at 25° is 7.2×10^{-4} (25); Neut. Eq. 120.5.

[Salts: $NH_4\bar{A}$, lfts. or hexag. tbls., sublimable (10); $Na\bar{A}$ (10); $K\bar{A}$, lfts. from alc. in which it is spar. sol. (1 pt. $K\bar{A}$ in 736.4 pts 99% alc. at 16.5° (5)) (use in sepn. of $\bar{C}$ from the isomeric α-chloroisocrotonic acid (3:1615) (4) (18) (17)); $Ag\bar{A}$, ndls., spar. sol. aq. (10) (17); $Ca\bar{A}_2$, pr. spar. sol. cold aq. (10) (17); $Ba\bar{A}_2$, more sol. aq. than $Ca\bar{A}_2$ (10) (17); $Cu\bar{A}_2$, blue ndls., converted by warm aq. to a basic salt (10); $Pb\bar{A}_2.H_2O$ (10).]

[$\bar{C}$ with NaOEt is unchanged even at 215° (20), but $\bar{C}$ with 10 N KOH at 100-200° decomposes with formn. of AcOH (1:1010), oxalic acid (1:0445), $CO_2 + H_2$ + other prods. (20).]

[For study of rate of reactn. of $\bar{C}$ with K_3AsO_3 see (2).]

[$\bar{C}$ with PCl_5 on warming gives (10) α-chlorocrotonoyl chloride, liq. with sharp odor, b.p. 112° (10).]

—— Methyl α-chlorocrotonate: b.p. 161–162° (see 3:5870). [For study of rate of esterification of $\bar{C}$ with MeOH see (26) (27).]

—— Ethyl α-chlorocrotonate: b.p. 176° (see 3:8523).

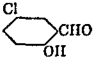
Ⓓ α-Chlorocrotonamide: lfts., spar. sol. cold aq., eas. sol. alc.; m.p. 113.5° (8), 111.5–112.5° (11), 107° (10). [From α-chlorocrotonyl chloride (above) (10) or ethyl α-chlorocrotonate (11) with conc. aq. NH_4OH; also by other routes such as from α,α,β-trichloro-*n*-butyraldehyde (3:5910) with NH_4OH + KCN (93% yield (8)).]

—— α-Chlorocrotonanilide: unreported.

—— α-Chlorocroton-α-naphthalide: unreported.

3:2700 (1) Stelling, *Z. physik. Chem.* **B-24**, 423 (1934). (2) Backer, van Oosten, *Rec. trav. chim.* **59**, 57–58 (1940). (3) Roberts, *J. Chem. Soc.* **1938**, [illegible]
3015–3040 (1910). (5) Wislicenus, *Ann.* **248**, 288, 293, [illegible]
1008–1010 (1887). (7) von Auwers, *Ber.* **56**, 724 (1923). [illegible]
1929, 1016. (9) Kahlbaum, *Ber.* **12**, 2338–2339 (1879). [illegible]
(11) Rambaud, *Bull. soc. chim.* (5) **1**, 1352–1355 (1934) [illegible]
1232 (1914). (13) Michael, Browne, *Am. Chem. J.* **9**, 2 [illegible]
J. Am. Chem. Soc. **36**, 2505 (1914). (15) Krämer, Pinner, *Ann.* **158**, 51 (1871). (16) Pinner, *Ber.* **8**, 1563 (1875). (17) Melikoff, *Ann.* **234**, 200, 203–204 (1886). (18) Michael, Schultess, *J. prakt. Chem.* (2) **46**, 256, 260–262 (1892). (19) Wallach, *Ber.* **10**, 1530 (1877). (20) Friedrich, *Ann.* **219**, 351–356, 371–373 (1883).
(21) Michael, Pendleton, *J. prakt. Chem.* (2) **38**, 4 (1888). (22) Wislicenus, *Ann.* **248**, 337 (1888). (23) Wallach, *Ann.* **173**, 301 (1874). (24) Valentin, *Ber.* **28**, 2661–2662 (1895). (25) Ostwald, *Z. physik. Chem.* **3**, 244 (1889). (26) Sudborough, Roberts, *J. Chem. Soc.* **87**, 1845–1846 (1905). (27) Michael, Oechslin, *Ber.* **42**, 322 (1909). (28) Long (to Wingfoot Corp.), U.S. 2,376,007, May 15, 1945; *C.A.* **39**, 3550 (1945).

3:2800 5-CHLORO-2-HYDROXY-BENZALDEHYDE (5-Chlorosalicylaldehyde)



$C_7H_5O_2Cl$ Beil. VIII-53 $VIII_1$—

M.P. 100°	(1)	B.P. 105° at 12 mm. (1)
99.5°	(2) (3) (4) (5) (11)	
99°	(6) (7)	
98°	(8)	
95–97° u.c.	(9)	

Colorless tbls. from alc.; long flat ndls. from C_6H_6 (1). — Insol. aq.; sol. alc., ether. — Sol. in alk. with yel. color.

[For prepn. of $\bar{C}$ from salicylaldehyde (1:0205) by chlorination with Cl_2 (10) (11) in AcOH (2), or with SO_2Cl_2 (1) (8), see indicated refs.; from 5-chloro-2-hydroxybenzyl alcohol by oxidn. with $K_2Cr_2O_7$ + H_2SO_4 see (6); from 5-chlorosalicylic acid (3:4705) by reduction (poor yield) see (3); from *p*-chlorophenol (3:0475) via Reimer-Tiemann reactn. (4) or via hexamethylenetetramine (7) see indicated refs.]

$\bar{C}$ on reduction with Raney Ni (Al/Ni alloy) in 10% aq. alk. at 90° gives (75% yield (16)) *o*-cresol (1:1400).

$\bar{C}$ on oxidn. with CrO_3 gives (in poor yield (1)) 5-chlorosalicylic ac. (3:4705), m.p. 172° (1).

$\bar{C}$ yields with satd. aq. $NaHSO_3$ soln. a cpd. $\bar{C}.NaHSO_3$ (12) (use in purification of $\bar{C}$ (4)). — $\bar{C}$ with NH_3 gives 5,5′,5″-trichloro-hydrosalicylamide, yel. scales from ether, m.p. unrecorded (10). — $\bar{C}$ in alk. gives on oxidn. with H_2O_2 good yield (13) of 4-chloropyrocatechol (3:2470).

C̄ in AcOH treated with conc. HNO_3 as directed (14) gives 5-chloro-3(?)-nitrosalicylaldehyde, yel. ndls. from et. pet., m.p 105–107° (14)

C̄ htd. with chloroacetic ac. (3:1370) and slightly more than 2 moles KOH in s t. at 160° yields (15) 4-chlorocoumarone (oil, volatile with steam) and 5-chloro-2-formylphenoxyacetic ac. (not volatile with steam from alk. soln.), cryst. from aq , m.p. 169–170° (15).

Ⓓ 5-Chlorosalicylaldoxime: ndls. from aq., m p. 128° (15) (7); 123–124° (9); 122°. (11) (6) [use in inorganic analysis (9)].

Ⓓ 5-Chlorosalicylaldehyde phenylhydrazone [Beil. XV-189]: m.p. 150–152° (15), 148° (11).

—— 5-Chlorosalicylaldehyde *p*-nitrophenylhydrazone: unreported.

—— 5-Chlorosalicylaldehyde 2,4-dinitrophenylhydrazone: unreported.

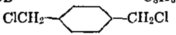
Ⓓ 5-Chlorosalicylaldehyde semicarbazone: ndls from AcOH, m.p. 286–287° (11) (4)

3:2800 (1) Durrans, *J. Chem. Soc* **123**, 1426 (1923) (2) Bradley, Dains, *Am. Chem. J.* **14**, 295 (1892). (3) Weil, Traun, Marcel, *Ber* **55**, 2665 (1922). (4) Sen, Ray, *J. Indian Chem. Soc.* **9**, 176 (1932). (5) Hanus, *J. prakt Chem.* **158**, 265 (1941) (6) Visser, *Arch Pharm* **235**, 547 (1897) (7) Duff, *J. Chem. Soc.* **1941**, 547–550. (8) Peratoner, *Gazz chim ital.* **28**, I, 235 (1898) (9) Flagg, Furman, *Ind. Eng. Chem., Anal. Ed* **12**, 529–531 (1940). (10) Piria, *Ann.* **30**, 169 (1839).

(11) Biltz, Stepf, *Ber.* **37**, 4024 (1904) (12) Bertagnini, *Ann* **85**, 196 (1853). (13) Dakin, *Am Chem. J.* **42**, 488 (1909). (14) Lovett, Roberts, *J. Chem Soc.* **1928**, 1978. (15) Stoermer, *Ann.* **312**, 325–326 (1900). (16) Schwenk, Papa, Whitman, Ginsberg, *J. Org Chem.* **9**, 1–8 (1944).

3:2825 *p*-XYLYLENE DICHLORIDE $C_8H_8Cl_2$ Beil. V - 384

(ω,ω′-Dichloro-*p*-xylene)



V_1-(186)

V_2-(300)

M.P. 100°	(1) (2)	B.P. 240–245° dec.		(2)
98–99°	(3)	135°	at 16 mm.	(1)
98–100°	(6)			

Lfts. or tbls. (from alc.). — Volatile with steam.

[For prepn. from *p*-xylylene glycol by distn. with conc. HCl see (4); for prepn. from benzyl chloride (3:8535) + trioxymethylene + $ZnCl_2$ see (1) (42% yield (6)); for prepn. of C̄ from *p*-xylene (1:7415) with SO_2Cl_2 + Br_2O_2 refluxed in sunlight 4 hrs. (58% yield) see (6).]

C̄ on htg. with 30 pts. aq. in s t. at 170–180° yields (1) (4) *p*-xylylene glycol [Beil. VI-919], ndls., very sol. aq., alc. or ether, m.p 112–113°.

C̄ boiled with $Pb(NO_3)_2$ soln. yields (5) terephthalaldehyde [Beil. VII-675], fine ndls. from boilg. aq., m p. 115°.

C̄ htd. with benzyl alc. (1:6480) + KOH gives good yield (1) of *p*-xylylene glycol dibenzyl ether, cryst. from alc , m p. 67° (1).

3:2825 ... -229 (1934) (2) Lauth, Grimaux, *Bull. soc. chim.* ... (3) Wislicenus, Penndorf, *Ber* **43**, 1838 (1910). ... Grimaux, *Compt. rend.* **83**, 825 (1876). (6) Kulka,

3:2855 2,3-DICHLOROBENZO-QUINONE-1,4
(*o*-Dichlorobenzoquinone)

$C_6H_2O_2Cl_2$

Beil. VII-632
VII₁—

M.P. 100–101° (1)
96–98° (2)
96° (3)
95–96° (4)

[*See also 2,3-dichlorohydroquinone* (3:4220).]

Yel. ndls. from aq. (2) or alc. (1). — $\bar{C}$ has characteristic quinone odor.

[For prepn. of $\bar{C}$ from 2,3-dichlorohydroquinone (3:4220) by oxidn. with MnO_2 + dil. H_2SO_4 (yields: 88% (1), 60% (3)) (4), or with CrO_3/AcOH (2) see indic. refs.; for formn. of $\bar{C}$ from *p*-benzoquinone (1:9025) in HCl or H_3PO_4 with Cl_2 see (6).]

[For study of oxidn.-reductn. potential of system $\bar{C}$ + 2,3-dichlorohydroquinone (3:4220) see (1) (5).]

[$\bar{C}$ with butadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloronaphthoquinone-1,4 (3:4857); similarly $\bar{C}$ with 2,3-dimethylbutadiene-1,3 gives an adduct which upon oxidn. yields (7) 2,3-dichloro-6,7-dimethylnaphthoquinone-1,4.]

[For use of $\bar{C}$ as accelerator for vulcanization of rubber see (8).]

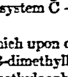
[$\bar{C}$ in alc. with *p*-nitrosodimethylaniline gives (60% yield (9)) corresp. nitrone; for condens. of $\bar{C}$ with other nitroso cpds. and use of prods. as dye intermediates see (10).]

[$\bar{C}$ in $CHCl_3$ with Cl_2 is not attacked at low temps., but at ord. temp. yields (4) tetrachloro-*p*-benzoquinone (chloranil) (3:4978).]

$\bar{C}$ on reductn. (presumably with SO_2 + H_2O) yields 2,3-dichlorohydroquinone (3:4220) q.v.

3:2855 (1) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2204–2205 (1923). (2) Eckert, Endler, *J. prakt. Chem.* (2) **104**, 82 (1922). (3) Peratoner, Genco, *Gazz. chim. ital.* **24**, II 375–396 (1894). (4) Oliveri-Tortorici, *Gazz. chim. ital.* **27**, II 584–585 (1897). (5) Kvalnes, *J. Am. Chem. Soc.* **56**, 668–669 (1934). (6) Chelintsev, *Compt. rend. acad. sci. (U.S.S.R.)* **14**, 289–291 (1937); *Cent.* **1937**, II 351; *C.A.* **31**, 7350 (1937). (7) I.G., Brit. 324,661, Feb. 27, 1930; French 677,236, March 6, 1930; French 677,781, March 14, 1930; *Cent.* **1930**, II 810. (8) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, I 3133. (9) Gündel, Pummerer, *Ann.* **529**, 31 (1937). (10) Gündel (to I.G.), Ger. 563,968, Nov. 11, 1932; *Cent.* **1933**, II 619.

3:2885 3,4,5-TRICHLOROPHENOL



$C_6H_3OCl_3$

Beil. VI —
VI₁—
VI₂-(181)

M.P. 101° (1) (4)
99–100° (2)
91° (3)

B.P. 271–277° u.c. at 746 mm. (3)

Ndls. from lgr. — Volatile with steam. — Ionization const. at 25° is 4.5×10^{-9} (4); $\bar{C}$ is too weakly acidic to be titrated (1) although sol. in alk.

[For prepn. from 3,4,5-trichloroaniline via diazo react. (51% yield) see (1) (2); by cleavage of 3,4,5-trichloroanisole see (3).]

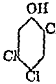
C̄ treated with large excess Br_2 yields 2,6-dibromo-3,4,5-trichlorophenol, ndls. from AcOH, m.p. 180° (3).

The methyl ether of C̄, 3,4,5-trichloroanisole, prepared indirectly, has m.p. 63° (3).

Ⓓ 3,4,5-Trichlorophenyl benzoate: from C̄ + BzCl + 20% NaOH; ndls. from alc., m.p. 120° (3).

3:2885 (1) Tiessens, *Rec. trav chim* **50**, 113 (1931) (2) Herzberg, Scharfenberg, Ger. 367,362, Jan. 20, 1923, *Cent.* **1923**, II 1254. (3) Kohn, Kramer, *Monatsh.* **49**, 163–165 (1928). (4) Tiessens, *Rec. trav chim.* **48**, 1066–1068 (1929).

3:2910 4,5-DICHLORO-2-METHYLPHENOL (4,5-Dichloro-*o*-cresol)



$C_7H_6OCl_2$ Beil. VI — VI_1-(174) VI_2-(333)

M.P. 101° (1)

Ndls. from pet. ether; spar. sol. pet. ether, eas. sol. alc., AcOH, C_6H_6.

[For prepn. of C̄ from 4-chloro-2-methylphenol (3:0780) with Cl_2 in $CHCl_3$ see (1).]

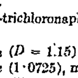
C̄ in 2 pts. ice-cold HNO_3 ($D = 1.48$) stood for 12 hrs. gives (75% yield (1)) a prod. of compn. $C_7H_4O_8N_3Cl_2$, white ndls. from dry ether by addn. of pet. ether, m.p. 110° dec. (1).

C̄ in AcOH on mononitration yields (1) 4,5-dichloro-6-nitro-2-methylphenol [Beil. VI_1-(179)], yel. ndls. from pet. ether, m.p. 69° (1)

Ⓓ 4,5-Dichloro-2-methylphenyl benzoate: ndls. from C_6H_6, m.p. 80–81° (1). [From C̄ in alk. soln. on shaking with benzoyl chloride (1).]

3:2910 (1) Zincke, *Ann.* **417**, 207, 231–233 (1918).

3:2935 2,3-DICHLORONAPHTHOL-1



$C_{10}H_6OCl_2$ Beil. VI-612 VI_1— VI_2—

M.P. 101° (1)

Subl. in ndls.; spar. sol. cold aq., mod. sol. hot aq.; eas. sol. alc., ether, AcOH, $CHCl_3$, C_6H_6.

[For prepn. from sodium 1-naphtholsulfonate-2 by htg. with PCl_5 at 100–120° see (1).]

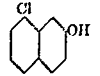
C̄ dis. in hot Na_2CO_3 yielding sol. Na salt.

C̄ htd. with PCl_5 at 130–140° yields 1,2,3-trichloronaphthalene (3:2125), colorless ndls. from alc, m p. 90° (1).

C̄ on oxidn. in s.t. at 200° with dil. HNO_3 ($D = 1.15$) yields (1) phthalic ac. (1:0820), converted in m.p. tube to phthalic anhydride (1·0725), m.p. 128° (1).

C̄ on oxidn. with CrO_3 in AcOH or dil. H_2SO_4 gives (although in poor yield (1)) 2,3-dichloronaphthoquinone-1,4 (3:4857), gold-yel. ndls. (from alc.), m.p. 190°.

3:2935 (1) Claus, Knyrim, *Ber.* **18**, 2926–2929 (1885).

3:2965 8-CHLORONAPHTHOL-2  $C_{10}H_7OCl$ Beil. VI - 649 VI₁— VI₂-(604)

M.P. 101° u.c. (1) **B.P.** 307–308° (1)
101° (2) (3) (5)

Ndls. from lgr.; very eas. sol. alc., ether, AcOH; C_6H_6, $CHCl_3$; spar. sol. pet. ether. — Volatile with steam. — Č depresses m.p. of 6-chloronaphthol-2 (3:3500) to 79–88° (5).

[For prepn. of Č from sodium 2-hydroxynaphthalenesulfonate-8 [Beil. XI-286, XI_1-(67)] with 2 moles PCl_5 at 150–160° see (1) (note that some 1,7-(2,8)dichloronaphthalene (3:1385) is also formed and that its proportion increases with more PCl_5 or at higher temps. (1)); from 8-aminonaphthol-2 [Beil. XIII-685] via diazotization and use of Cu_2Cl_2 reactn. see (2); for formn. of Č (20% yield (3)) from β-naphthol (1:1540) by treatment with soln. of $Na_2CO_3 + Cl_2$ see (3) (note that 30% of 2,2′-dihydroxybinaphthyl-1,1′ [Beil. VI-1051, VI_1-(519)] together with a tar is also formed (3)).]

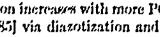
[Č (2 pts.) with benzaldehyde (1 pt.) with 7 pts. HBr/AcOH soln. stood for 24 hrs. gives (75% yield (2)) *meso*-phenyl-dichlorodibenzoxanthane, colorless ndls. from acetone, m.p. 213–214.5° (2).]

[Č (as sodium salt) treated with CO_2 under press. at elevated temp. as directed gives (4) 8-chloro-2-hydroxynaphthoic acid-3, pale yel. ndls. from hot C_6H_6, m.p. 250° (4).]

Ⓓ 8-Chloro-2-naphthyl *m*-nitrobenzoate: citron-yel. ndls. from hot C_6H_6 on addn. of 4 vols. hot alc., m.p. 176° (5). [From Č in warm dil. aq. NaOH on shaking with *m*-nitrobenzoyl chloride (5).]

3:2965 (1) Claus, Volz, *Ber.* 18, 3157–3158 (1885). (2) Dilthey, Quint, Heinen, *J. prakt. Chem.* (2) 152, 73–75 (1939)
II 767; *C.A.* 22, 339
Cent. 1933, II 446.

3:2990 *p*-CHLOROPHENACYL CHLORIDE (Chloromethyl *p*-chlorophenyl ketone) $C_8H_6OCl_2$ Beil. VII - 282 VII₁-(152)



M.P. 101–102° (2) **B.P.** 270° (1)
101° (1)

Ndls. (from alc.).

[For prepn. from *p*-chloroacetophenone (3:6735) by chlorination in CS_2 see (1); from chloroacetyl chloride (3:5235) + chlorobenzene (3:7903) + CS_2 + $AlCl_3$ see (2).]

Č on oxidn. with alk. $KMnO_4$ yields *p*-chlorobenzoic ac. (3:4940).

Č on treatment with Br_2 gives (3) ω-bromo-*p*-ω-dichloroacetophenone, cryst. from alc., m.p. 83–83.5° (3). — Č with KCN yields (4) *p*-chlorobenzoylacetonitrile, m.p. 129.5–130° (4). — Č with KSCN yields (4) *p*-chlorophenacyl thiocyanate, m.p. 138.6–139.2° (4). — Č with Na_2S at 60° gives (5) *bis*-(*p*-chlorophenacyl) sulfide, m.p. 121–121.6° (5).

Č in MeOH treated with $NH_2OH.HCl$ yields (6) corresponding oxime, chloromethyl *p*-chlorophenyl ketoxime, m.p. 100.5–101° (6). [Note that although this deriv. has m.p. too similar to that of original Č to be used as identification itself, upon htg. at 100° with conc. H_2SO_4 and pouring into aq. it is converted by Beckmann rearr. to chloroaceto-*p*-chloroanilide [Beil. XII-612], m.p. 168° (6), ndls. from alc., m.p. 169° (7).]

C̄ (1 mole) in alc. gradually added to phenylhydrazine (2 moles) in alc. with cooling ppts. (8) 1-phenyl-3-chlorophenyl-Δ^2-diazene-1,2, yel ndls. from alc., m.p. 164–164.5° (8).

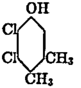
3:2990 (1) Gautier, *Ann. chim.* (6) **14**, 395–396 (1888). (2) Collet, *Compt. rend.* **125**, 718 (1897). (3) Rabcewicz-Zubkowski, *Roczniki Chem* **9**, 532–537 (1929); *C.A.* **24**, 92 (1930). (4) Rabcewicz-Zubkowski, Kaflinska, *Roczniki Chem.* **10**, 541–569 (1930); *C.A.* **25**, 505 (1931). (5) Chrzaszczewska, Chwalinski, *Roczniki Chem.* **7**, 67–73 (1927); *Cent.* **1927**, II 415; *C.A.* **22**, 1339 (1928). (6) Collet, *Bull. soc. chim.* (3) **27**, 540 (1902). (7) Beckurts, Frerichs, *Arch. Pharm.* **253**, 241 (1915). (8) Bodforss, *Ber.* **52**, 1762, 1772–1773 (1919).

CHAPTER VIII

DIVISION. A. SOLIDS

(3:3000–3:3499)

3:3005 5,6-DICHLORO-3,4-DIMETHYLPHENOL (5,6-Dichloro-*o*-4-xylenol)



$C_8H_8OCl_2$ Beil. S.N. 529

M.P. 102.5° (1)
102° (2)

Cryst. from lt. pet. — Very sol. most organic solvents. — Volatile with steam.

[For prepn. of $\bar{C}$ from 5,6-dichloro-3,4-dimethylaniline (5,6-dichloro-*o*-4-xylidine) (3) via diazotization and hydrolysis (yield not stated) see (1); for formn. of $\bar{C}$ from 4,5,6-trichloro-1,1-dimethylcyclohexen-4-one-3 with conc. H_2SO_4 at 110–120° (yield not stated) see (2).]

$\bar{C}$ with Cl_2 in lt. pet. readily gives (2) 2,5,6-trichloro-3,4-dimethylphenol (3:4747), m.p. 182°.

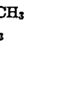
The nitration of $\bar{C}$ has not been reported, and the expected 2-nitro-5,6-dichloro-3,4-dimethylphenol is unknown.

—— 5,6-Dichloro-3,4-dimethylphenyl acetate: unreported.

Ⓓ 5,6-Dichloro-3,4-dimethylphenyl benzoate: m.p. 97.5° (1), 94° (2).

3:3005 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 2532–2533. (2) Hinkel, *J. Chem. Soc.* 125, 1851 (1924). (3) Hinkel, Ayling, Bevan, *J. Chem. Soc.* 1928, 1877.

3:3015 1,3,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V - 545
V_1-(263)
V_2-(446)

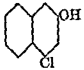
M.P. 103° (1) (2) (4)
102–103° (3)
94° (8)

[For prepn. of $\bar{C}$ from 1,3-dichloronaphthalenesulfonyl chloride-5 [Beil. XI-163] (4) (5), from 1,5-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (1), from 1-chloro-5-nitronaphthalenesulfonyl chloride-3 [Beil. XI-182] (6), or from 1-chloronaphthalene-3,5-*bis*-(sulfonyl chloride) [Beil. XI-215] (7), each with PCl_5 as directed, see indic. refs.; from 1,7-dichloronaphthylamine-3 (8) via diazotization and use of Cu_2Cl_2 reactn. see (8); for formn. of $\bar{C}$ (together with other products) from 1-nitronaphthalene [Beil. V-553, V_1-(264)] with Cl_2 (2) in pres. of $I_2 + FeCl_3$ (3) see indic. refs.]

[$\bar{C}$ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to K salt as directed (1) yields potassium 1,3,5-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 152° (1)).]

3:3015 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 253. (2) Atterberg, *Ber.* **9**, 317 (1878). (3) Buffle, Corbaz, *Arch. sci. phys. nat.* **14**, 149–158 (1932); *Cent.* **1932**, II 3394. (4) Widman, *Ber.* **12**, 2230 (1879). (5) Armstrong, Wynne, *Chem. News* **61**, 274 (1890). (6) Cleve, *Chem. Ztg.* **17**, 758 (1893). (7) Armstrong, Wynne, *Chem. News* **62**, 163 (1890). (8) Friedländer, Karamessinis, Schenk, *Ber.* **55**, 48–49 (1922).

3:3045 4-CHLORONAPHTHOL-2



$C_{10}H_7OCl$ Beil. S.N. 538

M.P. 104° (1)
103–104° (2)
102–103° (2)
100° (4)

Ndls. from lgr. or 30% aq. alc.

[For prepn of $\bar{C}$ from 1,4-dichloronaphthol-2 (3:3840) by partial reduction with $SnCl_2$ in AcOH/HCl at 100° in s.t. for 8 hrs (74% yield (2)) (1) see indic. refs., from 4-chloronaphthol-2-sulfonic acid-1 (2) (see also under 3:3840) by hydrolysis of the sulfonic acid group (91% yield) see (2); from 4-chloronaphthalene-1,2-diazo-oxide (itself obtd. in 95% yield (3) from 4-chloro-2-nitronaphthylamine-1 with HNO_2) on boilg. with Al powder in EtOH for 19 hrs. (84% yield (4)) or (less advantageously) with Na_2SnO_2 (4) see indic. refs.]

NaĀ is spar. sol. in cold aq 10% NaOH (4).

[$\bar{C}$ with alc. NaOH + $CHCl_3$ (3:5050) undergoes Reimer-Tiemann reaction giving (but in very small yield (2)) 4-chloro-2-hydroxynaphthaldehyde-1, m.p. 118° (2).]

$\bar{C}$ (in alk. soln.) with diazotized aniline gives (4) 4-chloro-1-benzeneazonaphthol-2, or-red ndls. from acetone, or crimson ndls. from chlorobenzene, m p. 165° (4) (note that after fusion and resolidification this prod. has m.p. 151° but after a second resolidification (at about 155°) remelts on slow htg. at 165° (4)). [For use of $\bar{C}$ in prepn. of azo dyes by coupling with *o*-hydroxydiazonium salts see (5).]

—— 4-Chloro-2-naphthyl methyl ether: pl. from lt. petroleum, m.p. 44–45° (4). [From $\bar{C}$ with Me_2SO_4 + aq. NaOH (4).]

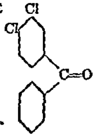
Ⓓ **4-Chloro-2-naphthyl acetate**: pl. from aq. MeOH or lt. petroleum, m.p. 58–59° (2), 56° (4) [From $\bar{C}$ with excess Ac_2O refluxed 30 min. (90–100% yield (2)).]

Ⓓ **4-Chloro-2-naphthyl benzoate**: ndls. from alc., m.p. 83–84° (2).

3:3045 (1) Fries, Schimmelschmidt, *Ann.* **484**, 293 (1930). (2) Burton, *J. Chem. Soc.* **1945**, 280–283. (3) Hodgson, Birtwell, *J. Chem. Soc.* **1943**, 322. (4) Hodgson, Birtwell, *J. Chem. Soc.* **1943**, 468–469. (5) Herzberg, Wunderlich (to I.G.), Ger. 459,889, May 18, 1928; *Cent.* **1928**, II 395; not in *C.A.*

3:3070 3,4-DICHLOROBENZOPHENONE

(3,4-Dichlorophenyl phenyl ketone)



$C_{13}H_8OCl_2$ Beil. S.N. 652

M.P. 104–105° (1)
102–103° (2) (3)

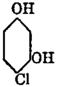
Cryst. (from alc. (1)).

[For prepn. (79.5% yield) from *o*-dichlorobenzene (3:6055) + BzOH (1:0715) + $AlCl_3$ see (1); for prepn. from *o*-dichlorobenzene (3:6055) + BzCl (3:6240) + $AlCl_3$ see (2) (3).]

Ⓓ **3,4-Dichlorobenzophenone oxime:** m.p. 153–154° (1). [This oxime upon Beckmann rearr. with H_2SO_4 gives (1) 3,4-dichlorobenzanilide which can be hydrolyzed to 3,4-dichlorobenzoic ac. (3:4925), m.p 207–208° (1), and aniline]

3:3070 (1) Newton, Groggins, *Ind. Eng. Chem.* **27**, 1398 (1935). (2) Böeseken, *Rec.* **27**, 15 (1908). (3) Kraay, *Rec. trav. chim.* **49**, 1085 (1930).

3:3100 4-CHLORORESORCINOL



$C_6H_5O_2Cl$ Beil. VI — VI_1— VI_2-(818)

M.P. 105° (1) (10)
102° (2)

B.P. 259.5° (2)
255–256° (4)
147° at 18 mm. (1)

The nature of the cpd., m.p. 89°, and formerly (3) thought to be C̄, is still in doubt, cf. (1).

C̄ is very sol. in aq. and *not* volatile with steam (1); eas. sol. aq., alc., ether, C_6H_6, and CS_2 (4).

[For prepn. of C̄ from resorcinol (1:1530) by actn. of SO_2Cl_2 in ether (95% yield (1)) see (1) (4).]

C̄ with $FeCl_3$ gives a blue-violet soln. becoming brown on warming (4).

C̄ reduces NH_4OH/$AgNO_3$ on warming (4).

C̄ on further chlorination with SO_2Cl_2 (no details) gives (96% yield (1)) of 4,6-dichlororesorcinol (3:3380).

C̄ (10 g.) refluxed with $KHCO_3$ (40 g.) in aq. (50 ml.) for 1½ hrs. gives (76% yield (5)) of 5-chloro-2,4-dihydroxybenzoic acid (6), cryst. from hot aq., m.p. 224–225° cor. (6), 215–216° (Maquenne bloc) after drying at 100–105° (5) (6).

C̄ in AcOH treated with xanthydrol (1:5205) yields 4-chloro-2-(?)-xanthydrylresorcinol, cryst. from C_6H_6, m p. 215° (7).

[For studies on prepn. of alkyl ethers of 4-chlororesorcinol for use as antiseptics and germicides see (8); for use of C̄ in prepn. of purpurin (1,2,4-trihydroxyanthraquinone) by reaction with phthalic anhydride, H_2SO_4 + H_3BO_3, see (9)]

[For coupling of C̄ with diazotized aniline, *p*-nitroaniline, or *p*-toluidine see (11).]

Ⓓ **4-Chlororesorcinol diacetate:** m.p. 46–47° (10).

Ⓓ **4-Chlororesorcinol dibenzoate:** m.p. 66° (10).

3:3100 (1) Moore, Day, Suter, *J.* [illegible]
J. Gen. Chem. (*U.S.S R.*) **3**, 164–171
J. Am. Chem. Soc. **55**, 319–320 (193[illegible]). [illegible]
(5) Fabre, *Ann. chim.* (9) **18**, 79–81 (1922). (6) Sandin, McKee. *J. Am. Chem. Soc.* **57**, 1077–1078 (1935). (7) Ref. 5, pp. 108–109. (8) Read (to Lambert Pharmacal Co.), U.S. 2,036,827, April 7, 1936; *Cent.* **1937**, I 697; *C.A.* **30**, 3592 (1936). (9) Lee, Buxbaum (to du Pont Co), U S. 1,985,452, Dec. 25, 1934; *Cent.* **1935**, II 439; *C.A.* **29**, 1104 (1935). (10) Petyunin, *J. Gen. Chem.* (*U.S.S.R.*) **14**, 203–210 (1944); *C.A.* **39**, 2285 (1945).
(11) Petyunin, *J. Gen. Chem.* (*U.S.S.R.*) **14**, 303–311 (1944); *C.A.* **39**, 4060 (1945).

3:3130 2-CHLOROHYDROQUINONE  $C_6H_5O_2Cl$ Beil. VI - 849
VI$_1$-(417)
VI$_2$-(844)

M.P. 106° (1) (2) (12)   B.P. 263° (1) (2)
105.5° cor. (3)
104° (4) (5)
103° (6)
102° (7)
101–102° (8)

[*See also 2-chlorobenzoquinone-1,4* (3:1100).]

Colorless lfts from $CHCl_3$ in which Č is eas sol. hot but spar. sol. cold. — Very eas. sol. aq., alc., or ether; sol. in warm C_6H_6 (*dif.* from hydroquinone (1:1590) and use in sepn. from latter (1)). — Not sublimable (5)

[For prepn. of Č from 2-chlorobenzoquinone-1,4 (3:1100) by reductn. with aq. SO_2 (2) (9) see indic. refs. (note, however, that in dil. aq NaOH under N_2 both reductn. and sulfonation occur (10)); from benzoquinone-1,4 (1:9025) with conc. HCl (11) (2) or in $CHCl_3$ with HCl gas (100% yield (12)) (2); from sodium benzoquinonesulfonate (5) with conc HCl below 20° (55% yield (5)) in CO_2 see indic. refs.; from *p*-benzoquinone dichloride (2,3-dichlorocyclohexen-5-dione-1,4) [Beil. VII-573] by reductn with $SnCl_2$ + HCl at 0° see (4); from hydroquinone (1:1590) in CCl_4 with Cl_2 see (13).]

[Č is used as a photographic developer under name "Adurol" (for identification of Č in developers see (1)); Č forms an addn. cpd. (14) with 2 moles *p*-(methylamino)phenol also used as developer under name Chloranol; for use of Č as vulcanization accelerator see (15); for use of Č as antioxidant (16) and as gum inhibitor in cracked gasoline (17) or in aq. emulsion as insecticidal spray (18) see indic. refs.; for study of bactericidal actn. see (19).]

Č on oxidn. with $NaClO_3$ + H_2SO_4 + V_2O_5 in AcOH (92% yield (20)), with $K_2Cr_2O_7$ + H_2SO_4 (yield: 89% (21), 84% (8)) (2), with MnO_2 + dil. H_2SO_4 (56% yield (8)), or with PbO_2 in C_6H_6 (22) gives 2-chlorobenzoquinone-1,4 (3:1100). [For studies of oxidn.-reductn. potential of this system and also for the intermediate quinhydrone see under the quinone (3:1100).]

[For reactn of Č with phthalic anhydride + conc. H_2SO_4 at 130–135° see (2); for reactn. of Č with naphthalene-1,2-dicarboxylic acid anhydride (23) or with naphthalene-2,3-dicarboxylic acid anhydride (24) each fused with $AlCl_3$ + NaCl see indic. refs.]

Č in AcOH with xanthydrol (1:5205) yields (25) 2-chloro-3-xanthydrylhydroquinone, cryst. from C_6H_6, m.p. 236–237° (25).

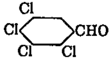
Č gives *no effervescence* with aq. 10% Na_2CO_3 but soln. darkens on stdg. (1); Č with aq. 5% $AgNO_3$ scarcely reduces in cold but does so rapidly on warming (1); Č with 10% aq. $FeCl_3$ gives red-brown color in cold and on boilg. pronounced quinone-like odor (1).

Ⓓ **2-Chlorohydroquinone diacetate:** pr. from dil. alc., m.p. 99° (1) (26), 72° (2), 71–72° (27), 70.5° cor. (3) [From Č with Ac_2O (2) or AcCl (26).] [Note that a monoacetate, m.p. 62° (28) has been reported, but the reason for the wide divergence in the m.p.'s reported for the diacetate has not been explained.]

Ⓓ **2-Chlorohydroquinone dibenzoate:** fine woolly ndls. from mixt. of alc. + ether, m.p. 130° (2). [From Č on refluxing with BzCl (2).]

Chem. Soc. **1934**, 680. (17) Betts, Hammett, *J. Am. Chem. Soc.* **59**, 1568–1572 (1937). (18) Kindler, *Ann.* **452**, 108 (1927). (19) Mehner, *J. prakt. Chem.* (2) **62**, 560–565 (1900). (20) Menon, *J. Chem. Soc.* **1936**, 1775–1777.
(21) Jenkins, *J. Am. Chem. Soc.* **55**, 2898 (1933). (22) Ivanov, *Bull. soc. chim.* (5) **4**, 686 (1937).

3:3140 2,3,4,5-TETRACHLOROBENZALDEHYDE $C_7H_2OCl_4$ Beil. S.N. 635



M.P. 106–106.5° (1)

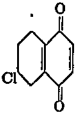
[For prepn. of C̄ from 2,3,4,5-tetrachlorobenzal (di)chloride (3:9397) by hydrolysis (presumably with strong H_2SO_4) see (1).]

C̄ with $NaHSO_3$ forms the corresp. addn. cpd. which may be used as means of sepn. of C̄ from 2,3,5,6-tetrachlorobenzaldehyde (3:2700).

[For use of C̄ in prepn. of dyestuffs see (1).]

3:3140 (1) Chem. Fabrik Griesheim-Elektron, Brit. 251,511, May 27, 1926; *Cent.* **1926**, II 2355; [*C.A.* **21**, 1361 (1927)]: French 603,650, April 20, 1926; *Cent.* **1926**, II 2355; not in *C.A.*

3:3145 6-CHLORONAPHTHOQUINONE-1,4 $C_{10}H_5O_2Cl$ Beil. S.N. 674

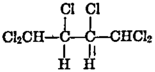


M.P. 106–107° (1)

[For prepn. of C̄ from benzoquinone-1,4 (1:9025) by addition of 2-chlorobutadiene-1,3 ("Chloroprene") (3:7080) and subsequent oxidation of the resulting Diels-Alder type adduct see (2); for formn. of C̄ by oxidation of various dichloronaphthalenes see (1).]

3:3145 (1) Kozlov, Talybov, *J. Gen. Chem.* **9**, 1827–1836 (1939); *C.A.* **34**, 4067 (1940). (2) Carothers, Collins (to du Pont Co.), U.S. 1,967,862, July 24, 1934; *Cent.* **1936**, I 2209; *C.A.* **28**, 5994–5995 (1934).

3:3155 1,1,2,3,4,4-HEXACHLOROBUTANE $C_4H_4Cl_6$ Beil. S.N. 10



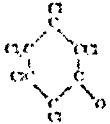
M.P. 107° (1) (2)

[For isolation of C̄ from the high-boilg. fraction resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1) (2); long refluxing (20 days) of freshly distilled samples of the latter compound also yields (1) C̄.]

C̄ on boilg. with alc. $Ca(OH)_2$ or with alk. at room temp. loses 2 HCl yielding (1) the liquid stereoisomer (3:6150) of 1,2,3,4-tetrachlorobutadiene-1,3. [The solid stereoisomer (3:0870) was *not* obtained from C̄ (1).]

3:3155 (1) Müller, Hüther, *Ber.* **64**, 589–600 (1931); *C.A.* **25**, 3956–3957 (1931). (2) Ghighi, *Ann. chim. applicata* **28**, 363–368 (1938); *Cent.* **1939**, I 86; *C.A.* **33**, 6792 (1939).

3:3180 HEXACHLOROCYCLOHEXADIENE-2,4-ONE-1 (Hexachloro-[illegible])



C_6OCl_6 Beil. VII - 144; VII_1-(96)

M.P. 107° (1) (3) (4)
106° (5) (6)

Cryst. from $CHCl_3$ or CS_2, white rods from pet. eth. (1) — [illegible] aq., spar. sol. cold alc., mod. sol. C_6H_6, very eas. sol. $CHCl_3$ or pet. eth. (4)

[For prepn. by various methods see Beil. VII-144 + Beil. VII_1-(96); for recent prepn. by chlorination of phenol see (2).]

Č with aq. KI (1) or Zn dust in boil. alc. (1), or $SnCl_2$ + HCl in AcOH (100% yield) (2) (5) or even with conc. aq. or alc. KOH (1) yields pentachlorophenol (3:4850).

Č (4 g.) [illegible] added to conc. HNO_3 (20 g.) with warm. [illegible] and the product [illegible] poured into aq. [illegible] recrystd. from nitrobenzene, yields (5) tetrachloro-p-benzoquinone (chloranil) (3:4250), m.p. 290° (5)

Č melted with conc. H_2SO_4 (then [illegible]) [illegible] with shaking until reaction suddenly begins, evolves HCl and on cooling [illegible] (see above) separates (2)

3:3180 (1) Barton, McCombie, J. Chem. Soc. 1931, 144. (2) Britton, Mattis, Alquist, Harold (to Dow Chem. Co.), U.S. 1,907,036, Aug. 7, 1934; Cent. 1935, I 2464. (3) Langer, Ann. 215, 121 (1882). (4) Hergesem, [illegible] 30, [illegible] (1903). (5) Biltz, Ber. 37, 4[illegible] (1904). (6) Biltz, Gemm, Ber. 37, 4 [illegible] 1904. (7) Tor[illegible] (to U.S. Rubber Co.), U.S. 2,279,257, June 12, 1942; C.A. 37, 4[illegible] (1943).

3:3200 1,5-DICHLORONAPHTHALENE

$C_{10}H_6Cl_2$ Beil. V - 543; V_1-(262); V_2-(440)

M.P. 107°	(1) (6) (7) (9) (10)
106.5-107°	(3)
106.5°	(2) (24)
106-107°	(4)
105-107°	(5)

Ltts. from alc. or AcOH. — Sublimes in very broad thin pr. — [For use as wood impregnant see (22).]

[For prepn. of Č from 1,5-dinitronaphthalene [Beil. V-558, V_1-(274)] (6) (2), from naphthalene-1,5-disulfonyl chloride [Beil. XI-212] (50% yield (4)) (7) (8), from 5-chloronaphthalene-1-sulfonyl chloride [Beil. XI-161] (9) (2), from 5-chloronaphthol-1 [Beil. VI-612] (10) by htg. with PCl_5, see indic. refs.; from 5-chloronaphthylamine-1 [Beil. XIV-741, XIV_1-(733)] by htg. corresp. diazonium salt with 2 moles PCl_5, see (1) (11); from 1,5-dichloro-7-aminonaphthalene by replacement of $-NH_2$ by $-H$ see (12); from 1,5-dichloronaphthalene-sulfonic acid-2 [Beil. XI-181] by hydrolysis of $-SO_3H$ group see (13) (14); from 4,5-dichloronaphthalene-2-sulfonyl chloride [Beil. XI-182] or from 1,5-dichloronaphthalene (3:2135) by htg. with conc. HCl in s.t. at 290° see (15); from naphthalene (1:7200) in CCl_4 at −10 to 0° with Cl_2 in pres. of Fe (together with other products) (16) or from 1-

nitronaphthalene [Beil. V-553, V_1-(264)] with Cl_2 (together with other products) (17) (2) see indic. refs.]

[C̄ in $CHCl_3$ soln. satd. with Cl_2 gives (25) both 1,5-dichloronaphthalene tetrachloride, m.p. 84°, and a trichloronaphthalene dichloride, m.p. 94° (separated by spar. soly. of latter in MeOH).]

[C̄ on mononitration yields (10) 1,5-dichloro-8-nitronaphthalene [Beil. V-556], yel. pr. from AcOH, m.p. 142° (10) (17) (23); note that the isomeric 1,5-dichloro-3-nitronaphthalene, m.p. 132°, has been reported indirectly (23) (12).]

[C̄ on monosulfonation (18) (13) gives chiefly 1,5-dichloronaphthalenesulfonic acid-3 [Beil. XI-183, XI_1-(41)] (corresp. sulfonyl chloride, m.p. 143° (13), corresp. sulfonamide, m.p. 204° (24)) accompanied by a smaller amt. 1,5-dichloronaphthalenesulfonic acid-2 [Beil. XI-181] (corresp. sulfonyl chloride, m.p. 125° (13)).]

[C̄ with picric acid yields a cpd. C̄.PkOH, m.p. 87° (10).]

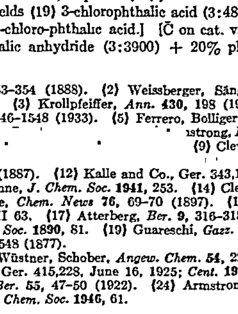
[C̄ on oxidn. with CrO_3/AcOH yields (19) 3-chlorophthalic acid (3:4820) but on oxidn. with dil. HNO_3 yields (20) a nitro-chloro-phthalic acid.] [C̄ on cat. vapor-phase oxidn. (21) gives 80% yield 3-chlorophthalic anhydride (3:3900) + 20% phthalic anhydride (1:0725).]

3:3200 (1) Erdmann, *Ann.* **247**, 353–354 (1888). (2) Weissberger, Sängewald, Hampson, *Trans. Faraday Soc.* **30**, 890 (1934). (3) Krollpfeiffer, *Ann.* **430**, 198 (1923). (4) Beattie, Whitmore, *J. Am. Chem. Soc.* **55**, 1546–1548 (1933). (5) Ferrero, Bolliger, *Helv. Chim. Acta* **11**, 1146–1147 (192[illegible] ...strong, *Ber.* **15**, 205 (1882). (8) Armstrong, Wyn[illegible] (9) Cleve, *Bull. soc. chim.* (2) **26**, 540 (1876).

(11) Erdmann, *Ber.* **20**, 3185–3186 (1887). (12) Kalle and Co., Ger. 343,147, Oct. 28, 1921; *Cent.* **1922**, II 143. (13) Turner, Wynne, *J. Chem. Soc.* **1941**, 253. (14) Cleve, *Chem. Ztg.* **17**, 398 (1893). (15) Armstrong, Wynne, *Chem. News* **76**, 69–70 (1897). (16) B.A.S.F., Ger. 234,912, May 26, 1911; *Cent.* **1911**, II 63. (17) Atterberg, *Ber.* **9**, 316–318, 926–928 (1877). (18) Armstrong, Wynne, *Proc. Chem. Soc.* **1890**, 81. (19) Guareschi, *Gazz. chim. ital.* **17**, 120 (1887). (20) Atterberg, *Ber.* **10**, 547–548 (1877).

(21) Pongratz, Bassi, Fuchs, Süss, Wüstner, Schober, *Angew. Chem.* **54**, 22–25 (1941). (22) Röchling'sche Eisen und Stahlwerke, Ger. 415,228, June 16, 1925; *Cent.* **1925**, II 1239. (23) Friedländer, Karamessinis, Schenk, *Ber.* **55**, 47–50 (1922). (24) Armstrong, Wynne, *Chem. News* **61**, 274 (1890). (25) Wynne, *J. Chem. Soc.* **1946**, 61.

3:3220 PARA-α-CHLORO-ISOBUTYRALDEHYDE (2,4,6-*tris*-(α-Chloro-isopropyl)-trioxane-1,3,5) $C_{12}H_{21}O_3Cl_3$ Beil. XIX - 391 XIX_1—



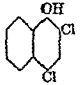
M.P. 107° (1) (2)

Odorless tasteless ndls. (from distn. with steam); pr. (from ether); insol. aq.; sol. alc., ether, pet. ether. — Sublimes above m.p.

[For prepn. from α-chloro-isobutyraldehyde (3:7235) by shaking with ½ vol. conc. H_2SO_4 see (1) (2).]

3:3220 (1) Brochet, *Ann. chim.* (7) **10**, 357–359 (1897). (2) Brochet, *Bull. soc. chim.* (3) **7**, 643–644 (1892).

3:3250 2,4-DICHLORONAPHTHOL-1 $C_{10}H_6OCl_2$ Beil. VI - 612
VI₁-(308)
VI₂-(582)



M.P. 107–108° (2) (3)
106–107° (1) (5)

Ndls. (from dil. alc or lgr); from AcOH C̄ separates in pr. with 1 mole of AcOH rapidly lost at 40–50° (1). — C̄ is volatile with steam; eas. sol. abs. alc. ether or C_6H_6. — C̄ on htg. to 180° decomposes with loss of HCl.

[For prepn. from β-naphthol (1:1500) (1) (2) or 4-chloronaphthol-1 (3:3720) (4) by chlorination see (1) (2) (3); from naphthalene 1,2,3,4-tetrachloride (3:4750) by oxidn. with CrO_3 in AcOH see (5); for other methods see Beil. VI-612]

C̄ dissolves in NaOH or Na_2CO_3 but on warming (or even long stdg. in cold) yields (6) ultramarine flocks which impart to ether a violet, and to benzene a deep blue violet, color (6). [Same result obtd. with $K_3Fe(CN)_6$ but not with pyridine (6).]

C̄ on boil. with dil. HNO_3 is oxidized (1) to phthalic ac. (1:0820); but with CrO_3 in AcOH yields 2-chloronaphthoquinone-1,4 (3:3580), volatile with steam, golden-yel. ndls from aq., alc., or AcOH, m.p. 116° (1).

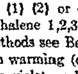
C̄ is not affected by Sn + alc. HCl (3), or Na/Hg (3), but on htg. in AcOH with conc. HI (D = 1.7) for 10 hrs. gives (3) α-naphthol (1:1500).

C̄ dislvd. in 20 pts. 15% aq. KOH and shaken with 4 pts. $(CH_3)_2SO_4$ gives (94% yield (3)) of the methyl ether, methyl 2,4-dichloro-1-naphthyl ether, colorless ndls. from alc., m p. 58° (3).

D **2,4-Dichloro-1-naphthyl acetate:** from C̄ by htg. with AcCl (2); ndls. (from alc.), m.p. 74–76° (2).

3:3250 (1) *Cleve, Ber.* **21**, 891–893 (1888) (2) Zincke, *Ber.* **21**, 1035–1036 (1888). (3) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 384–385 (1921/22). (4) Reverdin, Kauffmann, *Ber.* **28**, 3053 (1895). (5) Helbig, *Ber.* **28**, 506 (1895). (6) Willstätter, Schuler, *Ber.* **61**, 370 (1928).

3:3275 6-CHLORO-2-METHYL-BENZOIC ACID $C_8H_7O_2Cl$ Beil. S.N. 941



M.P. 108° (1)
102° (2)
[91.5° (3)]

Long slender colorless ndls. from hot aq. (2) or from HCl (1).

[For prepn. of C̄ from 6-chloro-2-methylbenzamide (see below) (itself obtd. from 6-chloro-2-methylbenzonitrile, m p. 82–83° (2)) by actn. of nitrous acid see (2); from 6-amino-2-methylbenzoic acid (1) via diazotization and use of Cu_2Cl_2 reactn. see (1) (3).]

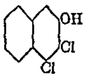
C̄ on htg. with aniline, K_2CO_3, and copper powder yields (1) 3-methyldiphenylamine-carboxylic acid-2, cryst. from 50% alc., m.p. 145° dec. (1).

[C̄ melted and treated with Br_2 evolves HBr, and the prod. on warming with dil. NaOH yields (3) 3-chloro-α-hydroxyphthalide, colorless pl. from dil. alc., m p. 138° (3).]

—— **6-Chloro-2-methylbenzamide:** scales from boilg. aq., m.p. 167° (2). [Prepd. indirectly as above.]

3:3275 (1) Gleu, Nitzsche, *J. prakt. Chem.* (2) **153**, 213 (1939). (2) Kenner, Witham, *J. Chem. Soc.* **119**, 1458 (1921). (3) Levy, Stephen, *J. Chem. Soc.* **1930**, 2788.

3:3295 3,4-DICHLORONAPHTHOL-2



$C_{10}H_6OCl_2$ Beil. VI —
VI$_1$—
VI$_2$-(604)

M.P. 108° (1) (2).

Small colorless ndls. from lgr. Sol. in cold K_2CO_3 soln. (2).

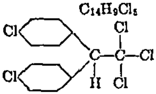
[For prepn. from β-naphthol (1:1540) via 1-nitrosonaphthol-2, chlorination with SO_2Cl_2 in tetrachloroethane to 1-nitroso-3,4-dichloronaphthol-2, reduction to 1-amino-3,4-dichloronaphthol-2 and thence via diazo reaction to C̄ see (1); for prepn. from 1,3,4-trichloronaphthol-2 by reduction with $FeSO_4$ + NaOH see (2).]

C̄ treated with 1 mole HNO_2 yields 1-nitroso-3,4-dichloronaphthol-2, golden-yel. cryst. from AcOH, m.p. not given (1).

3:3295 (1) Marschalk, *Bull. soc. chim.* (4) **43**, 1367 (1928). (2) Herzberg, Spengler, Schmidt (to I.G.), Ger. 431,165, June 30, 1926; *Cent.* **1926**, II 1196.

3:3298 1,1,1-TRICHLORO-2,2-*bis*-(*p*-CHLOROPHENYL)ETHANE (" DDT ", " *p,p*-DDT ")

$C_{14}H_9Cl_5$ Beil. S.N. 479



M.P.	**108.5–109**	(26)
	108–109°	(1) cor. (27) (29)
	108°	(2) (28)
	107–108° cor.	(3)
	107°	(4)
	106–107°	(17)
	105–106°	(5)
	105°	(6)

[*See also* 1,1-*dichloro*-2,2-*bis*-(*p-chlorophenyl*)*ethane*, " *DDD* " (3:3320).]

Note that C̄ is the remarkable insecticide to which so much publicity is currently being given. Despite the general fanfare the amount of real scientific data which has been released at this writing is small, although very rapid publication is inevitable in the near future. No attempt can be made in this text to cover the utilization of C̄, but attention is drawn to two bibliographies (7) (8) containing respectively 174 and 418 references, although most of these are to general and nontechnical reports. For an extensive review of chemistry of C̄ see (30).

[For patents on utilization of " DDT " as insecticide see (9) (10). — For studies of toxicology and pharmacology of " DDT " see (11) (12) (13) (14). — Note that C̄ is by rabbits in part excreted as di-(*p*-chlorophenyl)acetic acid (3:4612), m.p. 166–166.5° u.c. (24).]

Colorless cryst. from 95% alc. — C̄ is spar. sol. in 95% alc.; viz., 0.8 wt. % at 0°, 3.9 wt. % at 48° (3); spar. sol. pet. ether of b.p. 30–60° (3); C̄ is moderately sol. in CCl_4, ether, or $CHCl_3$ (3); eas. sol. in pyridine, dioxane, C_6H_6, or acetone (3); for data and graph of *wt. % solubility/temp.* over range 0–48° see (3) cf. (25); for soly. of C̄ in kerosenes see (31). [For detn. of C̄ in technical samples, i.e., in pres. of " DDD " (3:3320), by recrystn. from satd. alc. soln. of " DDT " see (26).]

Note that technical C̄ may contain some of the isomeric 1,1,1-trichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)ethane (3:1820) and/or polymers of chloral (3:5210); in fact, technical C̄ *of setting point* 88° *contains* about 70% C̄ accompanied by 18% of the *o-p* isomer + 6% of the *o,o'* isomer (25). — For extensive report on the compn. of technical grade C̄ see (29).

{*For optical crystallographic props. of* C̄ *see* (28).}

PREPARATION OF C̄

C̄ is universally prepd by condensation of chloral or chloral hydrate with chlorobenzene.

From chloral hydrate. {For prepn. of C̄ from chloral hydrate (3:1270) with chlorobenzene (3:7903) + fumg H_2SO_4 (8–10% SO_3) (70% yield (2) (4)) or $ClSO_3H$ (77% yield (32)) see indic. refs}

From chloral. {For prepn. of C̄ from anhydrous chloral (3:5210) with chlorobenzene (3:7903) + conc. H_2SO_4 see (6) (15) (16).}

CHEMICAL BEHAVIOR OF C̄

Reduction of C̄. C̄ on reduction with Na/alc. gives up all its chlorine quant. detn. of which comprises a method for the quant. detn. of C̄ (14)

{C̄ on hydrogenation with H_2 + Pd/$CaCO_3$ in various solvents on slight warming gives according to conditions (18) various products of bimolecular reduction; these include 2,2,3,3-tetrachloro-1,1,4,4-tetra-(*p*-chlorophenyl)butane, cryst. from AcOEt, m.p. 271.5° (28% yield (18)), both higher-melting (229°) and lower-melting (174°) stereoisomers of 2,3-dichloro-1,1,4,4-tetra-(*p*-chlorophenyl)butene-2 (former 36% yield, latter in traces) (18), and perhaps other products; for much further study of these reaction products see the original reference (18)}

{C̄ *on electrolytic reduction in alc. HCl soln. gives* (13% *yield* (19)) *at the cathode* 1,1,4,4-tetra-(*p*-chlorophenyl)butyne-2, pr. from AcOEt, m.p 174° (19); note that this prod. on oxdn. with CrO_3/AcOH gives (91% yield (19)) 4,4'-dichlorobenzophenone (3:4270), *m p* 145°.}

Oxidation of C̄. Attempts to oxidize C̄ with CrO_3/AcOH have given (5) no identifiable products.

Dehydrochlorination of C̄. [illegible] *ions can be caused to split out* 1 HCl yielding 1,1-[illegible]

C̄ with alc. [illegible] 15–20 min. (21) (for study of rate see (20) (27)) *gives* (*yi*[illegible] (21), 81% (5)) *1,1-dichloro-bis-(p-chlorophenyl)ethylene* (3:2438) {for use of this reaction by detn. of ionized chlorine as means for detn. of C̄ in spray deposit see (21)}

C̄ *with excess* $Ba(OH)_2 \cdot 8H_2O$ *in ethylene glycol refluxed* 10–12 *hrs. gives* (33% *yield* (24)) di-(*p*-chlorophenyl)acetic acid (3:4612), m.p. 166–166.5° u.c ; this results by initial loss of HCl as above and further degradation.

C̄ *in the pres. of minute amts.* (*e.g.*, 0.01%) *of* $FeCl_3$ *or* $AlCl_3$ *at* 110–120° *loses* HCl giving (22) cf. (34) 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:2438). (See also below under behavior of C̄ with $AlCl_3$ + C_6H_6.)

SUBSTITUTION REACTIONS OF C̄

Bromination. No study of the behavior of C̄ toward Br_2 appears yet to have been reported.

Chlorination. C̄ in CCl_4 soln. with Cl_2 + trace of PCl_3 in light at b p. of mixture for 3 hrs. gives (73% yield (5)) 1,2,2,2-tetrachloro-1,1-*bis*-(*p*-chlorophenyl)ethane (3:2477), m.p. 91–92° (5).

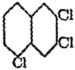
Nitration. C̄ on introduction of two nitro groups (no details) gives (6) a prod., ndls. from alc., m.p. 148.0–148.3° (29), which is presumably 1,1,1-trichloro-1,2-*bis*-(4-chloro-2-nitrophenyl)ethane; note that this *dinitro* compd. has same m.p. as corresp. dinitro deriv. from "*o,p*-DDT" (3:1820) but m.p. of a mixt. of the two is depressed (29).

C̄ on tetranitration with a mixt. (1:1 by volume) of fumg. HNO_3 and conc. H_2SO_4 at 100° for 1 hr. gives (23) 1,1,1-trichloro-2,2-*bis*-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 223.5–224.5° cor. (23). — [Note that similar tetranitration of "DDD" (1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethane (3:3320) gives (23) 1,1-dichloro-2,2-*bis*-(4-chloro-3,5-dinitrophenyl)ethane, m.p. 224.5–225.5° cor. (23); similar tetranitration of the *o-p* isomer of "DDT" (viz., 1,1,1-trichloro-2-(*o*-chlorophenyl)ethane) (3:1820) gives a prod., m.p. 229.5–230° cor. (23). — For color reactions of these tetranitro derivs. with MeOH/NaOMe and its use in detn. of C̄ see (23) (33).]

Behavior with $AlCl_3$ + C_6H_6. C̄ with anhydrous $AlCl_3$ (1 mole) in large excess of C_6H_6 reacts at room temp. evolving 2 moles HCl and giving (10% yield (1)) 1,1,2,2-tetraphenylethane [Beil. V-739, V_1-(371), V_2-(673)], m.p. 211°. [Note that the mechanism of this surprising result has not yet been explained; that by similar treatment the same tetraphenylethane is also obtd. in 25% yield from 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)-ethane (3:3320), in 10% yield from 1,1,1-trichloro-2,2-diphenylethane (3:1420), and from the *o-p* isomer of "DDT" (viz., 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethane) (3:1820), but *not* at all from 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:2438); and that if chlorobenzene is substituted for C_6H_6 no tetraphenylethane results from any of them (1).]

3:3298 (1) Fleck, Preston, Haller, *J. Am. Chem. Soc.* **67**, 1419–1420 (1945). (2) Darling, *J. Chem. Education* **22**, 170 (1945). (3) Gunther, *J. Am. Chem. Soc.* **67**, 189–190 (1945). (4) Iris, [illegible] 5, 71–74 (1944); *C.A.* **39**, 495 (1945). (5) [illegible] –156 (1945). (6) Zeidler, *Ber.* **7**, 1181 (187[illegible] and Plant Quarantine, 12 pp. (June [illegible] pp. (May 1945). [illegible] 056 (1944). (10) [illegible] 504 [illegible] ize, [illegible] ohl- [illegible] *em.* [illegible] 28, [illegible]) Brand, Bausch, [illegible], *J. prakt. Chem.* [illegible] 328 (1942). [illegible], Haller, *J. Am.* [illegible]

3:3300 2,3,5-TRICHLORO-NAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V-546 V_1— V_2—

M.P. 109.5° (1) (2)

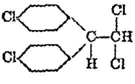
[For prepn. of C̄ from 2,3-dichloronaphthol-8 (3:4315) (2) or from 2,3-dichloronaphthalenesulfonyl chloride-8 [Beil. XI-164] (1) (2) (3) with PCl_5 see indic. refs.]

[C̄ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to salts as directed (1) gives salts of 2,3,5-trichloronaphthalenesulfonic acid-8 (corresp sulfonyl chloride, m.p. 164° (1)).]

3:3300 (1) Turner, Wynne, *J. Chem Soc.* **1941**, 247, 255–256. (2) Armstrong, Wynne, *Chem. News* **61**, 275 (1890). (3) Armstrong, Wynne, *Proc. Chem. Soc.* **1890**, 83; **1895**, 79

3:3320 1,1-DICHLORO-2,2-*bis*-(*p*-CHLOROPHENYL)ETHANE ("DDD"; "*p,p'*-DDD")

$C_{14}H_{10}Cl_4$ Beil. S.N. 479



M.P. 109.5–110° (3)
109.4–110.2° cor. (5)
108.5–110° (4)

This compd is closely related to "DDT" (3:3298) and occurs (4) as minor impurity in technical grades of this compound.

[For prepn of C̄ from dichloroacetaldehyde (3:5180) or from 2,2-dichloro-1-(*p*-chlorophenyl)ethanol (4) with chlorobenzene (3:7903) + conc. H_2SO_4 + fumg. H_2SO_4 (63% yield) see (4).]

C̄ with alc. KOH refluxed 3 hrs. loses 1 HCl giving (77% yield (4)) (5) 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:1430).

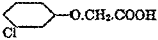
C̄ on dinitration with 10 vols fumg HNO_3 at 50° for ½ hr. gives (90% yield (4)) a dinitro deriv.; cryst from alc, m.p. 178–179° (4).

C̄ on tetranitration with a mixt. (1:1 by volume) of fumg. HNO_3 + conc. H_2SO_4 at 100° for 1 hr. gives (1) a prod., m.p. 224.5–225.5° cor, which presumably has the structure 1,1-dichloro-2,2-*bis*-(4-chloro-2,6-dinitrophenyl)ethane.

C̄ with anhydrous $AlCl_3$ (1 mole) + excess C_6H_6 at ord. temp. evolves HCl and gives (25% yield (2)) 1,1,2,2-tetraphenylethane, m.p. 211° (2).

3:3320 (1) Schechter, Haller, *J. Am Chem Soc.* **66**, 2129–2130 (1944). (2) Fleck, Preston, Haller, *J Am. Chem. Soc.* **67**, 1419–1420 (1945). (3) Cristol, Hayes, Haller, *Ind. Eng. Chem., Anal. Ed.* **17**, 470–473 (1945). (4) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc* **67**, 1596, 1600 (1945). (5) Cristol, *J. Am. Chem. Soc.* **67**, 1494–1498 (1945).

3:3325 *m*-CHLOROPHENOXYACETIC ACID $C_8H_7O_3Cl$ Beil. S.N. 522

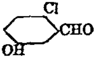


M.P. 110° (1) Neut. Eq. **186.5**
109.7–110.2° cor. (2)

[For prepn. from *m*-chlorophenol (3:0255) by htg with chloroacetic ac. (3:1370) and aq. alk. see (1) (2).]

3:3325 (1) Koelsch, *J. Am. Chem. Soc.* 53, 304–305 (1931). (2) Hayes, Branch, *J. Am. Chem. Soc.* 65, 1555–1557 (1943)

3:3350 6-CHLORO-3-HYDROXYBENZALDEHYDE (2-Chloro-5-hydroxybenzaldehyde)



$C_7H_5O_2Cl$ Beil. VIII — $VIII_1$-(526)

M.P. 111° (1)
110.5–111.5° (2)

Colorless ndls. from dil. AcOH (1). — Very slowly volatile with steam (1). — C̄ has pronounced sternutatory props. (1) (3).

[For prepn. from *m*-hydroxybenzaldehyde (1:0055) via direct chlorination see (2); via 4-nitro-3-hydroxybenzaldehyde, reductn. to corresp. amino cpd., and use of appropriate diazo reactn. see (1); for prepn. from *o*-chlorobenzaldehyde (3:6410) via nitration to 2-chloro-5-nitrobenzaldehyde, m.p. 78–79°, oximation, reduction to 2-chloro-5-aminobenzaldoxime, m.p. 159–160°, and finally diazotization and hydrolysis see (1); for prepn. from 4-chloro-3-methylphenol (3:1535) see (3); for prepn. from *p*-chlorophenol (3:0475) by condensation with chloral (3:5210) and subsequent alk. hydrolysis see (4).]

C̄ in 50% AcOH mononitrated as specified (1) gives mixt. of 2-nitro and 4-nitro products eas. sepd. by volatility of latter with steam (1): 2-Nitro-6-chloro-3-hydroxybenzaldehyde: yel. ndls. from dil. AcOH, m.p. 136° (5), 138° (3). [Corresp. *p*-nitrophenylhydrazone, deep or.-red ndls. from AcOH, m.p. 256–257° dec. (5); semicarbazone, yel. ndls. from alc., m.p. 249–250° dec. (5).] *4-Nitro-6-chloro-3-hydroxybenzaldehyde: deep yel. ndls. from AcOH*, m.p. 104° (5) (3). [Corresp. *p*-nitrophenylhydrazone, brick-red ndls. from AcOH, m.p. 284–286° dec. (5); semicarbazone, yel. pl. from alc., m.p. 266–267° dec. (5).]

C̄ in aq. contg. $NaHCO_3$ treated (1) with Me_2SO_4 yields 6-chloro-3-methoxybenzaldehyde, m.p. 62° (1). [Corresp. oxime, ndls., m.p. 101.5° (1); *p*-nitrophenylhydrazone, old-gold ndls., m.p. 229° (1).] [This methyl ether on oxidn. with $KMnO_4$ (1) yields 6-chloro-3-methoxybenzoic acid, ndls. from dil. AcOH, m.p. 170–171° (1).]

Ⓓ 6-Chloro-3-hydroxybenzaldoxime: colorless ndls. of monohydrate from dil. alc., from abs. alc. in anhydrous ndls., m.p. 146–147° (1).

—— 6-Chloro-3-hydroxybenzaldehyde phenylhydrazone: unrecorded.

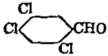
Ⓓ 6-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: red ndls. from dil. alc., m.p. 250–251° (1).

—— 6-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone: unrecorded.

Ⓓ 6-Chloro-3-hydroxybenzaldehyde semicarbazone: pale yel. ndls., m.p. 236° (1).

3:3350 (1) Hodgson, Beard, *J. Chem. Soc.* 1926, 151–154. (2) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; *Cent.* 1931, I 159; *C.A.* 24, 5768–5769 (1930). (3) Friedländer, Schenck, *Ber.* 47, 3046–3047 (1914). (4) Hsakh, Smola, Austrian 141,159, March 25, 1935; *Cent.* 1935, II 439. (5) Hodgson, Beard, *J. Chem. Soc.* 1926, 2034.

3:3375 2,4,5-TRICHLOROBENZALDEHYDE



$C_7H_3OCl_3$ Beil. VII-238 VII_1—

M.P. 112–113° (1)
110–111° (2)

Colorless ndls. from conc. alc. soln. (1). — Insol. boilg. aq. but volatile with steam. — Eas. sol. alc., ether, C_6H_6, $CHCl_3$, CS_2.

[For prepn. of C̄ from 2,4,5-trichlorobenzal (di)chloride (3:6910) by hydrolysis with fumg. H_2SO_4 (1), with warm conc. H_2SO_4 (3), or with aq. in s.t. at 260° (2) see indic. refs.]

[C̄ on oxidn. with $KMnO_4$ should yield 2,4,5-trichlorobenzoic acid (3:4630), m.p. 164°, but this reaction is not actually reported in the literature; note that C̄ in air oxidizes only slowly (1).]

[C̄ with Na_2SO_3 under press. gives (4) 5-chlorobenzaldehydedisulfonic acid-2,4 [Beil. XI-325].]

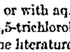
[C̄ with anhydrous NaOAc on htg. (Perkin synthesis) gives (1) 2,4,5-trichlorocinnamic acid, m.p. 200–201°.]

[For use of C̄ in prepn. of dyestuffs see (5) (3).]

—— 2,4,5-Trichlorobenzaldoxime: unreported.
—— 2,4,5-Trichlorobenzaldehyde phenylhydrazone: unreported.
—— 2,4,5-Trichlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.
—— 2,4,5-Trichlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

3:3375 (1) Seelig, *Ann.* 237, 147–149, 151 (1887). (2) Beilstein, Kuhlberg, *Ann.* 152, 238–239 (1869). (3) Fischer, Ger. 25,827, June 23, 1883, *Friedländer* 1, 42 (1877–87). (4) Geigy and Co., Ger. 198,909, June 1, 1908, *Cent.* 1908, II 214; [*C.A.* 2, 2733–2734 (1908)]. (5) Perkin, Clemo (to British Dyestuffs Corp.), Brit. 165,658, July 28, 1921, *C.A.* 16, 835 (1922).

3:3380 4,6-DICHLORORESORCINOL $C_6H_4O_2Cl_2$ Beil. VI - 820
VI₁-(403)
VI₂-(819)



M.P. 113.2° (1) (2)
112–113° (3)
108–109° (4)

Cryst. from lgr. — C̄ is very sol. aq. (forms hydrate, m.p. 70°) (1); C̄ is eas. sol. alc., ether (1). — [For bactericidal action of C̄ see (3).]

[For prepn. of C̄ from resorcinol (1:1530) with *N,N'*-dichlorourea see (1); from 4-chloro-resorcinol (3:3100) with SO_2Cl_2 (96% yield) see (3) cf. (4); (the prods. of m.p. 77°, b.p. 249° (5), and m.p. 101°, b.p. 254° (6), may have been impure samples of C̄).]

[C̄ with *N,N'*-dichlorourea + KBr gives (2) 2-bromo-4,6-dichlororesorcinol, m.p. 101°.]

[C̄ with *N,N'*-dichlorourea + KI gives (7) 2-iodo-4,6-dichlororesorcinol, m.p. 54°.]

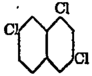
[C̄ with ethyl *α*-ethoxyacetoacetate in alc. NaOEt gives (4) 6,8-dichloro-3-ethoxy-[illegible]-7-hydroxycoumarin, m.p. 236°.]

Note that C̄ does *not* (6) (9) condense with phthalic anhydride.

Ⓓ 4,6-Dichlororesorcinol dimethyl ether: ndls. from alc., m.p. 118° (6), 117–118° (7), 116–117° (3). [From C̄ with Me_2SO_4 + aq. alk. (3) (9).]

3:3380 (1) Likhosherstov, *J. Gen. Chem.* (*U.S.S.R.*) 3, 164–171 (1933); *Cent.* 1934, I [illegible]; *C.A.* 28, 1675 (1934). (2) Likhosherstov, *J. Gen. Chem.* (*U.S.S.R.*) 3, 172–17[illegible]; *Cent.* 193[illegible] [illegible] ...ter, *J. Am. Chem. Soc.* [illegible] [illegible]

3:3400 1,3,7-TRICHLORONAPHTHALENE $C_{10}H_5Cl_3$ Beil. V-545
V_1—
V_2—



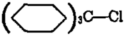
M.P. 113° (1) (2) (3)
112.5–113° (4)

Ndls. from alc.

[For prepn. of C̄ from 1,3-dichloronaphthalenesulfonyl chloride-7 [Beil. XI-183] (5), from 1,7-dichloronaphthalenesulfonyl chloride-3 [Beil. XI-182] (6), from 3,7-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 3-chloronaphthalene-1,7-*bis*-(sulfonyl chloride) [Beil. XI-215] (7), from 7-chloronaphthalene-1,3-*bis*-(sulfonyl chloride) [Beil. XI-212] (1) (3) (6) (7), from 1-nitronaphthalenedisulfonic acid-3,7 [Beil. XI-216] (3) (4), or from 7-chloro-3-naphtholsulfonic acid-1 (2), each with PCl_5 as directed, see indic. refs.; for formn. of C̄ from β-chloronaphthalene tetrachloride (1,2,3,4,6-pentachlorotetralin) [Beil. V-493] with alc. KOH see (8).]

[C̄ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to sodium salt as directed (1) yields sodium 1,3,7-trichloronaphthalenesulfonate-7 (corresp. sulfonyl chloride, m.p. 138° (1).]

3:3400 (1) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 253–254. (2) Battegay, Silbermann, Kienzle, *Bull. soc. chim.* (4) **49**, 718–719 (1931). (3) Armstrong, Wynne, *Chem. News* **61**, 93 (1890). (4) Alén, *Ber.* **17**, Referate, 437 (1884). (5) Armstrong, Wynne, *Chem. News* **61**, 275 (1890). (6) Armstrong, Wynne, *Chem. News* **76**, 69 (1879). (7) Armstrong, Wynne, *Chem. News* **62**, 165 (1890). (8) Armstrong, Wynne, *Chem. News* **61**, 285 (1890).

3:3410 α-CHLOROTRIPHENYL-METHANE 

$C_{19}H_{15}Cl$ Beil. V-700
V_1-(346)
V_2-(615)

(Triphenylchloromethane; triphenylmethyl chloride; trityl chloride)

M.P. 113° (1)
112–113° (2) (3); cor. (8)
112° (4) (5) (6) (46)
111–112° (7) (9)
111° (10) (11)
110.5–112° (12)
110–112° (13)
110.0–110.5° (14)
109.2° (15)
109° (16)
109–110° (17)
108–112° (18)
108–111° (19)
106–109° (20)
106° (21) (50)
105–109° (30)

B.P. [310° at 20 mm. (22)]
230–235° at 20 mm. (23)

Colorless (12) or pale greenish-yellow (7) (8) cryst. from hexane + AcCl (1), dry ether (9), lgr. (7) (8), or dry C_6H_6 + pet. ether (12) (17). — Ord. C̄ frequently conts. two kinds of crysts., white and yellow, both melting at 110–112° (13). — C̄ from CCl_4 cryst. with

1 mole solvent; Č from acetone cryst. with ½ mole solvent; in both cases solvent is lost at 92° but not readily in air at ord. temp. (24). — [For study of x-ray crystallography of Č see (25).] — Note that Č cannot be recrystd. from MeOH or EtOH without more or less complete conversion to the corresp. trityl ethers (see also below under behavior of Č with alcohols).

Č may be stored satisfactorily in ord. *screw-top bottles, provided they are well sealed* with paraffin (7) — On long exposure to moist air, however, Č is hydrolyzed (see also below) to triphenylcarbinol (1:5985), m p. 161–162°; for f p./compn. diagram of system Č + triphenylcarbinol, eutectic, m.p. 100°, contg. 90% Č, see (26). — Samples of partially hydrolyzed Č may be purified by recrystn. from ½ wt. of C_6H_6 contg. 5–25% acetyl chloride, the latter reconverting the triphenylcarbinol to Č (7).

Č is eas sol. in ether, C_6H_6 (100 g. C_6H_6 dis. 85.8 g. Č at 25° (35)), CCl_4, $CHCl_3$, or CS_2, but is much less sol. in pet. ether (19). — Solns. of Č in acetyl chloride (27) (29), benzoyl chloride (27), hot 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (27) (28), dichloroethylene (28), nitrobenzene (27), $SOCl_2$ (27), SO_2Cl_2 (29) are yellow; for study of effect of temp see (27) — Solns. of Č in liq. SO_2 are also yellow (29) and conduct electric current (30) (31) (32); for study of molecular weight of Č in liq SO_2 see (33). — Č is very sparingly sol. in liq. NH_3 but soln conducts elect. current (34).

[The protracted arguments on the constitution of Č and of trityl derivatives in general (controversy over carbonium and quinonoid forms, etc.) cannot be detailed within the scope of this book; however, for leading references since 1920 see (36) (37) (38) (39) (40) (41) (42) (43) (44) (45); for earlier references see Beil. V-700]

PREPARATION OF Č

The two best-studied preparations of Č are those from triphenylcarbinol (1:5985) with AcCl (3:7065) in C_6H_6 (93–95% yield (12)) and from CCl_4 (3:5100) with C_6H_6 + $AlCl_3$ (84–86% yield on $AlCl_3$ used (7) (8)). Note, however, that many other methods have also been used as recorded below.

From triphenylcarbinol (1:5985). [For prepn. of Č from triphenylcarbinol with AcCl (3:7065) *directly* (79% *yield* (46)) or in C_6H_6 soln. (93–95% *yield* (12)); with oxalyl (di)chloride (3:5060) (47); with HCl gas in dry C_6H_6 (48) (for study of equilibrium see (49)) contg. $CaCl_2$ (9) or in dioxane at 50° for 22 hrs. (86% yield (14)); with conc. HCl in AcOH (79% yield (50)) or in C_6H_6 + $ZnCl_2$ (85% yield (51)); with PCl_5 directly (52) or in lgr. (53) or in C_6H_6 (29) or in C_6H_6 + $ZnCl_2$ (90% yield (51)); with PCl_3 + $ZnCl_2$ in C_6H_6 (92% yield (51)); with $SOCl_2$ in C_6H_6 (97% yield (51)); with $SiCl_4$ in C_6H_6 or lgr. at 40° (54), or with $COCl_2$ (3:5000) in C_6H_6 + $CaCl_2$ (5) see indic. refs.]

From other triphenylcarbinol derivatives. [For prepn. of Č from K triphenylcarbinolate with $COCl_2$ (3:5000) *in toluene* (5); *from triphenylmethoxy—MgBr*, $(C_6H_5)_3C$—OMgBr (from benzophenone + C_6H_5MgBr), with AcCl in C_6H_6 (37% yield (55)) or with $COCl_2$ in toluene (14% yield (55)); from triphenylcarbinol ethyl ether (see also below) with $AlCl_3$ in CS_2 (56) or with AcCl (46) (57) see indic. refs.]

From various other trityl derivatives and relatives. [For prepn. of Č from α-bromotriphenylmethane (*trityl bromide*) with AgCl in C_6H_6 in s.t. at 200° *for several days* (50% yield (57)); from α-aminotriphenylmethane (tritylamine) [Beil. XII-1343, XII₁-(557)] with NH_4Cl in liq. NH_3 (34), from triphenylmethylphosphinic acid $[(C_6H_5)_3C(PO)(OH)_2]$ with PCl_5 (3 *moles*) at 70° (91% yield (20)); from triphenylmethane (1:7220) with PCl_5 at 160° for 2 hrs. (65% yield (58)) or with NOCl at 150° (59) see indic. refs.]

[For prepn. of Č from triphenylacetyl chloride [Beil. IX-713, IX₁-(309)] by loss of CO on htg. at 120–150° (60) or at 170–180° (61); from *bis*-(triphenylmethyl) peroxide [Beil.

VI-716, VI_1-(350)] with Cl_2 + a little I_2 in boilg. CCl_4 soln. for 3 hrs. (40% yield (23)) see indic. refs.]

From benzene with various polyhalogenated methanes. [For prepn. of C̄ from C_6H_6 (1:7400) with CCl_4 (3:5100) in pres. of $AlCl_3$ (84–86% yield on $AlCl_3$ used (7) (8); 70–85% yield (18)) cf. (62) (63) (64) in CS_2 (97% yield (19)) see indic. refs.; for use of $FeCl_3$ (31% yield against 77% with $AlCl_3$ under otherwise same conditions (10) cf. (65)) see indic. refs.]

[For prepn. of C̄ from C_6H_6 (1:7400) with $CHCl_3$ (3:5050) + $AlCl_3$ at 50° see (22).]

[For formn. of C̄ from C_6H_6 with dichloro-difluoro-methane (" Freon ") + $AlCl_3$ see (66).]

From various chlorotoluenes. [*For formn. of C̄ from benzotrichloride (3:6540) with* C_6H_6 in pres. of metallic U (67), Ti (68), Ce (69), or Cr (21) see indic. refs.; from benzal (di)chloride (3:6327) with C_6H_6 + $AlCl_3$ see (22).]

From various chlorodiphenylmethanes. [For formn. of C̄ from α-chlorodiphenylmethane (benzohydryl chloride) (3:0060) (22) or from α,α-dichlorodiphenylmethane (benzophenone chloride) (3:6960) (70) with C_6H_6 + $AlCl_3$ see indic. refs.]

From other miscellaneous sources. [For formn. of C̄ from pentaphenylethane [Beil. V-755, V_1-(386), V_2-(711)] with PCl_5 at 170° for 2 hrs. or refluxed in C_6H_6 (58), or (together with other products) with HCl at 150° (71) or on evapn. of soln. in SO_2Cl_2 (72).]

CHEMICAL BEHAVIOR OF C̄

Pyrolysis of C̄. C̄ on htg. at 200° (52) (73) or 250° (53) or at 150° in pres. of P_2O_5 (74) loses HCl and yields both triphenylmethane (1:7220), m.p. 92°, and 9-phenylfluorene [Beil. V-720, V_1-(355), V_2-(630)], m.p. 147–148°; note that 9-phenylfluorene is also formed from C̄ in various other reactions such as with $POCl_3$ on distn. (23) or with 1/10 wt. of mossy zinc refluxed in C_6H_6 for 5 hrs. (75).

Reduction of C̄. *C̄ is reduced to triphenylmethane by many different types of reducing* agent [e.g., C̄ in anhydrous formic acid (1:1005) at 100° evolves CO_2 + HCl and gives (yield: 79% in 30 min., 90% in 2 hrs. (4)) triphenylmethane (1:7220); C̄ in EtOH treated with conc. H_2SO_4 at 70–80° gives (76) (17) triphenylmethane accompanied by acetaldehyde (1:0100); C̄ is reduced by diethyl ether in the presence of $AlCl_3$ (56) (77), $FeCl_3$ (65), or $ZnCl_2$ (78) to triphenylmethane (1:7220), acetaldehyde (1:0100) and ethyl chloride (3:7015) also being formed; other reagents which effect reduction of C̄ to triphenylmethane (1:7220) include hydrazobenzene in boiling C_6H_6 (79), cyclohexadiene-1,3 (dihydrobenzene) + $HgCl_2$ (80); Zn + AcOH (50) (reaction here is complex, and various other prods. may be formed according to conditions), and dry H_2S at 150° (81)].

Oxidation of C̄. C̄ is *not* readily oxidized: C̄ with silver oxide in dry C_6H_6 or ether gives (78) a little fuchsone, $(C_6H_5)_2{=}C_6H_4{=}O$ [Beil. VII-520, VII_1-(290)], m.p. 168°, together with other amorphous products difficult to purify; note, however, that C̄ in alcohol-free acetone with $KMnO_4$ in same solvent instantly reduces the $KMnO_4$ and gives (100% yield (85)) triphenylcarbinol (1:5985).

Hydrolysis of C̄. C̄ with aq. hydrolyzes to triphenylcarbinol (1:5985) + HCl: e.g., C̄ on shaking with aq. at ord. temp. is 85% hydrolyzed in 48 hrs. (26) cf. (82) (83) (*in this connection note m.p./compn. diagram* (26) of C̄ + *triphenylcarbinol*); C̄ with boilg. aq. rapidly and completely yields only triphenylcarbinol.

[For study of hydrolysis of C̄ by aq. in acetone (84), in dioxane (14), or by aq. HCl (35) see indic. refs.]

C̄ dissolves in cold conc. H_2SO_4 yielding (86) (48) (87) a golden-yellow soln. with evolution of HCl (88) (86) (48) and formn. of triphenylcarbinyl hydrogen sulfate; dilution of this soln. with aq. ppts. (99% yield (86) (48)) triphenylcarbinol (*1:5985*).

[C̄ dissolves in phenol with deep brown color; on dilution of the freshly prepd. soln. with aq. it becomes colorless and both HCl and triphenylcarbinol are detectable; if, however, the phenol soln. has stood for some time prior to dilution some *p*-tritylphenol [Beil. VI-731, VI_1-(364)], m.p. 282°, is also formed (89) (see also below under behavior of C̄ with phenols).]

BEHAVIOR OF C̄ WITH OTHER INORGANIC REACTANTS

With Salts of Various Inorganic Acids

With Salts of Hydrogen Peroxide

[C̄ in acetone with 30% H_2O_2 in freezing mixt. treated with 50% KOH gives (90) trityl hydroperoxide, $(C_6H_5)_3C—O—OH$ (isolated as its addn. cpd. with pyridine hydrochloride, viz., $(C_6H_5)_3C—O—OH.C_5H_5N.HCl$, cryst. from alc., m.p. 133° dec.), accompanied by some triphenylcarbinol (1:5985).]

[C̄ in C_6H_6 with aq. Na_2O_2 as directed (91) gives (5–11% yield) *bis*-trityl peroxide, $(C_6H_5)_3C—O—O—C(C_6H_5)_3$, cryst. from hot CS_2, m.p. 185–186°, accompanied by much triphenylcarbinol; the *bis*-trityl peroxide is also obtainable from the trityl hydroperoxide (above) by reaction with C̄ in C_6H_6 on addn. of aq. alk. (90).]

With Salts of Halogen Hydrides

With alkali or alkaline-earth salts. [C̄ with alkali fluorides seems not to have been studied; note, however, that trityl fluoride, cryst. from CCl_4, m.p. 104° (6), has been prepd. by other means, viz., from triphenylcarbinol with HF (6) or with acetyl fluoride (85).]

[C̄ with anhydrous $CaBr_2$ in C_6H_6 at room temp. for 5–6 hrs. (92) or C̄ with HBr in C_6H_6 at room temp. for 20 hrs. (92) is largely converted to trityl bromide [Beil. V-704, V_1-(348), V_2-(617)], m.p. 152°.]

[For study of rate of reaction of C̄ with KI in dry acetone at 0° see (93); note, however, that, although trityl iodide [Beil. V-706], m.p. 132°, is doubtless formed, yet more or less sepn. of I_2 and formn. of triphenylmethyl (or its reaction prods.) occurs also.]

With metal chlorides. C̄ with many metallic chlorides forms double salts [e.g., C̄ with $AlCl_3$ forms (19) (87) a cpd., C̄.$AlCl_3$, dark-yellow very hygroscopic cryst. from nitrobenzene + CS_2, dec. abt. 122–125°; C̄ in nitrobenzene with $SnCl_4$ gives on addn. of dry CS_2 or.-yel. cryst. of a cpd., C̄.$SnCl_4$ (30) (57) (87) (94); C̄ with $SbCl_5$ gives (57) a cpd., C̄.$SbCl_5$, red cryst.; C̄ with BCl_3 gives a cpd., C̄.BCl_3 (6), etc.].

With Salts of Hydrogen Sulfide

[C̄ with alc. NaSH (from alc. NaOEt satd. with H_2S) (81) cf. (95) (96), or C̄ with KSH in C_6H_6 (96), gives triphenylthiocarbinol [Beil. VI_1-(352)], cryst. from abs. alc. or alc. + $CHCl_3$, m.p. 107° (81) (95). — C̄ with alc. Na_2S as directed gives (21% yield (95)) *bis*-trityl sulfide, m.p. 182° dec. — Note also that *bis*-trityl disulfide, cryst. from C_6H_6 + pet. ether, m.p. 157° dec. (95) [Beil. VI_1-(353)], is also known but prepd. indirectly (81) (95) (96).]

With Other Salts of Inorganic Acids

[C̄ with Ag_2SO_4 in liq. SO_2 (23), C_6H_6 (97), or at 120–130° for 15–20 min. (98) cf. (48) gives di-trityl sulfate [Beil. VI-717, VI_1-(351)]. — C̄ with $AgClO_4$ in nitrobenzene + C_6H_6 gives (99) trityl perchlorate [Beil. VI-717, VI_1-(351)]. — C̄ with $AgCrO_4$ in C_6H_6 gives (48) cf. (100) di-trityl chromate [Beil. VI-717]; note that this salt is also obtd. from C̄ with CrO_3 in C_6H_6 or CCl_4 (101).]

[C̄ with NaN_3 in C_6H_6 refluxed 20 hrs. gives (100% yield (102)) trityl azide [Beil V-708, V_1-(349), V_2-(618)], colorless cryst., m.p. 64° (102), 65° (103). — For study of reaction of C̄ with silver hyponitrite and decompn. of the transient trityl hyponitrite see (104).]

With Metal Oxides

[C̄ with HgO in dry C_6H_6, ether, CS_2, or $CHCl_3$ as directed (78) cf. (105) (106) gives (50–85% yield (78)) di-trityl oxide, cryst. from xylene, m.p. 237–238° (106), 235–237° (78) (105). — Note that C̄ with Ag_2O in C_6H_6 undergoes oxidation (cf. above); note that C̄ with CrO_3 in C_6H_6 or CCl_4 gives (101) di-trityl chromate [Beil. VI-717].]

With Metals

With alkali metals (or their amalgams). [C̄ in dry ether with 1% Na/Hg on shaking at room temp. (2) (8) (107) (108) (109) or C̄ with Na in liq. NH_3 (112) gives tritylsodium (sodium triphenylmethyl) [Beil. XVI_1-(589)]. C̄ with K in liq. NH_3 gives (112) tritylpotassium. — C̄ in dry ether with excess Li/Hg, Rb/Hg, or Cs/Hg in absence of air gives (113) corresp. trityllithium, tritylrubidium, or tritylcesium. — For behavior of C̄ with calcium in liq. NH_3 see (112). — In this connection note that C̄ in dry ether, C_6H_6, or CS_2 in absence of air and under CO_2 with molecular Ag (91) cf. (117), Hg (91), Zn (91) (114) (115), or C̄ with Cu bronze in C_6H_6 + EtOAc (116) or in s.t. at 80–110° in dark (117) gives triphenylmethyl (trityl); note also that C̄ with Zn + AcOH in the cold gives (50) triphenylmethane (1:7220) + trityl, but the same mixture if heated gives triphenylmethane + 1-benzohydryl-4-tritylbenzene [Beil. V-761], m.p. 231° (118), 230° cor. (119), the latter under certain conditions attaining as high as 70% (50) (118).]

With Zn. [C̄ with $\frac{1}{10}$ wt. of mossy zinc refluxed in C_6H_6 for 5 hrs. gives (75) 9-phenylfluorene (see also above under pyrolysis of C̄). — For behavior of C̄ with Zn in EtOAc see (120).]

With Mg (in dry ether). C̄ with Mg in dry ether in the pres. of I_2 as directed gives (96% yield (13)) cf. (121) of corresp. R—Mg—Cl cpd., viz., trityl—Mg—Cl [Beil. XVI-942, XVI_1-(556)]. — [The former controversy as to whether this can exist in a more reactive quinonoid structure (α) or a relatively less reactive carbonium (β) structure cannot be reported here (for references see above Beilstein citation), nor can space be taken for a full account of its reactions.] — Note, however, that this RMgCl cpd. with CO_2 gives (yields: 91% (2), 87.5% (121)) (122) (59) triphenylacetic acid [Beil. IX-712, IX_1-(309)], m.p. 264–265° dec. (122); for study of adverse influence of triphenylcarbinol or of benzaldehyde see (121).

With Nitrogenous Inorganic Reactants

[C̄ dislvd. in C_6H_6 and satd. with dry NH_3 gas (123) (124) repeatedly (125), or C̄ in naphthalene with dry NH_3 gas at 130° (126), gives (45% yield (126)) tritylamine (triphenylmethyl-amine) [Beil. XII-1343, XII_1-(557)], pr. from abs. alc., m.p. 102° (126), 103–104° (124), 105° (127) (corresp. B.HCl, spar. sol. aq., m.p. 244° (127)).]

[C̄ with NH_2OH (from NH_2OH.HCl in MeOH/NaOMe) in C_6H_6 gives (73–75% yield (3)) (128) cf. (129) *N*-tritylhydroxylamine [Beil. XV-33, XV_1-(11)], pr. from C_6H_6/pet. ether, m.p. 130–135° (3), 124–135° u.c. (128); for study of rearr. of this prod. see (129). — For study of *N*-methyl ether of this prod., viz., *N*-trityl-*N*-methylhydroxylamine (similarly prepd. from C̄ with *N*-methylhydroxylamine) see (130) (131); for study of the isomeric O-methyl ether, viz., *N*-trityl-O-methylhydroxylamine (from C̄ with methoxyamine), see (132).]

[C̄ with hydrazine hydrate (2 moles) in alc. at ord. temp. (232) or in dry ether under reflux (233) or in dry pyridine at 45–50° (234) gives (63% yield (234)) *N*,*N'*-di-tritylhydra-

zine (α,α'-hydrazotriphenylmethane) [Beil. XV-582, XV_1-(184)], m.p. 212° (234), 219–220° dec. (235), often accompanied (232) (233) by some *N*-tritylhydrazine [Beil. XV-581, XV_1-(184)]]

BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

With Organic Hydroxy or Mercapto Compounds

With Alcohols

$\bar{C}$ with alcohols gives the corresp. ethers of triphenylcarbinol. With the lower monohydric alcs this conversion can occur merely on solution and warming, but higher alcs. usually require htg., use of metal alcoholate, use of an acid acceptor (pyridine), etc.

With methyl alcohol. $\bar{C}$ with MeOH (1:6120) in C_6H_6 for 10 min. (133), or $\bar{C}$ with MeOH/NaOMe refluxed 4 hrs. (134), gives (55% yield (134)) triphenylcarbinyl methyl ether (α-methoxytriphenylmethane), cryst. from MeOH, m.p. 83.5–84° (133), 82.5–83° (134), 82.6–82.9° (134) (136), 82° (64); note, however, that this product exists in dimorphous forms; the lower-melting form just mentioned sometimes (134) (135) changes to a higher-melting form, m.p. 96.0–96.5° (134) (135); note also that the m.p. of this *methyl* ether is close to that of the *ethyl* ether (see below) but that a mixed m.p. of the two is depressed (136). — [For studies of hydrolysis of the methyl trityl ether to triphenylmethane (1:7220) and formaldehyde (1:0145) see (134) (136); for prepn. of its addn. cpd., m.p. 90–91°, with PkOH see (138)]

With ethyl alcohol. $\bar{C}$ with abs. EtOH (1:6130) on warming (1) (4) (5) (52) or even shaking 1 min. at ord. temp. (139), or $\bar{C}$ with abs. EtOH/NaOEt (9) (56) (134) (139), gives (yields: 83% (138), 50% (134)) triphenylcarbinyl ethyl ether (α-ethoxytriphenylmethane), cryst. from abs. alc., ether, or pet. ether, m.p. 84° (5), 83° (1) (9), 81.2–81.8° (134), 81.3° (56), 81° (4) — Note that the m.p. of this prod. is almost identical with that of triphenylcarbinyl methyl ether (above) but that a mixed m.p. of the two is depressed (137). — [For study of pyrolysis of this ethyl trityl ether yielding triphenylmethane (1:7220) and acetaldehyde see (134) (136); for study of its cleavage with AcCl (3:7065) (57) (46), with $AlCl_3$ in CS_2 (56), or with EtOH/HCl (26) see indic. refs.; for conversion with boilg. anhydrous formic acid to triphenylmethane (1:7220) see (4).]

With other monohydric alcs. [$\bar{C}$ with *n*-PrOH (1:6150) in dry pyridine at room temp. for 20 hrs. (140), or $\bar{C}$ with *n*-PrOH/NaO *n*-Pr refluxed 4 hrs. (134), gives (10% yield (134)) trityl *n*-propyl ether, cryst. from *n*-PrOH/pet. ether, m.p. 55° (140), 50.5–52.5° (134). — $\bar{C}$ with isopropyl alc. (1:6135) in dry pyridine at room temp. for 20 hrs. (140) or $\bar{C}$ with isopropyl alc/Na isopropylate under reflux gives (50% yield (134)) trityl isopropyl ether, m.p. 113° (140), 112.9–113.8° (134), 111.7° (56). — $\bar{C}$ with *n*-BuOH (1:6180) + sodium *n*-butylate gives (40% yield (134)) trityl *n*-butyl ether, oil, b.p. 196–198° at 5 mm. (134). — For prepn. of corresp. trityl ethers from *sec*.-butyl alc (1:6155) (134), isobutyl alc. (1:6165) (134), isoamyl alc. (1:6200) (134), cetyl alc. (1:5945) (140), allyl alc. (1:6145) (140), benzyl alc. (1:6480) (134), cyclohexanol (1:6415) (140), see indic. refs.]

[For prepn. of corresp. trityl ethers from *l*-menthol (1:5940) (152) (153) (154), *d*-borneol (1:5990) (152) (153), or cholesterol (1:5975) (152) see indic. refs.]

[Note, however, that $\bar{C}$ with K triphenylcarbinolate does *not* give the expected prod. but rather (96) *p*-hydroxytriphenylcarbinol in the form of its anhydride fuchsone; the expected ditrityl ether has been obtd. from $\bar{C}$ by action of HgO (see above).]

With various important substituted monohydric alcohols. [$\bar{C}$ with β-methoxyethanol (methyl "cellosolve") (1:6405) in pyridine gives (80–85% yield (141)) trityl β-methoxyethyl ether, m.p. 105.5–106.0° u.c. (141), 104° (142). — $\bar{C}$ with β-ethoxyethanol ("cellosolve") (1:6410) in pyridine at 100° for 5 hrs. gives (92% yield (141)) trityl β-ethoxyethyl

ether, m.p. 79.0–79.5° u c. (141), 77–78° (143). — C̄ with β-isopropoxyethyl alc. (isopropyl "cellosolve") (1:6413) in pyridine gives (50–60% yield (141)) trityl β-isopropoxyethyl ether, m.p. 71.0–71.5° u c. (141). — C̄ with β-benzyloxyethyl alc. (benzyl "cellosolve") (1:6533) in pyridine gives (50–70% yield (141)) trityl β-benzyloxyethyl ether, m.p. 76–77° u.c. (141). — C̄ with β-phenoxyethyl alc. (phenyl "cellosolve") (1:6518) in pyridine gives (75–85% yield (141)) trityl β-phenoxyethyl ether, m.p. 123.5–124.0 u.c. (141).]

[C̄ with β-(β-methoxyethoxy)ethyl alc. (methyl "carbitol") (1:6458) in pyridine gives (55–60% yield (141)) trityl β-(β-methoxyethoxy)ethyl ether, m.p. 58–59° u.c. (141). — Note that the trityl ethers of β-(β-ethoxyethoxy)ethyl alc. ("carbitol") (1:6470) and of β-(β-n-butoxyethoxy)ethyl alc. (butyl "carbitol") (1:6517) are unreported.]

With various polyhydric alcohols. (For C̄ with carbohydrates see separate section below.)

[C̄ with ethylene glycol (1:6465) in pyridine may according to conditions (141) give either or both of the two possible ethers, viz., ethylene glycol monotrityl ether, m.p. 105–105.5° u c. (141), 104.5–105.5° (144), 102–103° (143), 98–100° (140) (corresp. benzoyl deriv. m.p. 58 5–59 5° (144); corresp. p-nitrobenzoyl deriv., m p. 155–156° (144)), and/or ethylene glycol ditrityl ether, m.p. 190° u.c. (145), 187–188° u.c. (141), 185–186° (140)]

[C̄ with propylene glycol (propanediol-1,2) (1:6455) in pyridine gives (146) propylene glycol ditrityl ether, m.p. 176 5–177.0° u.c. (146).]

[C̄ (2 moles) with diethylene glycol (1:6525) in pyridine gives (60–70% yield (141)) diethylene glycol ditrityl ether, m.p. 157.5–158.0° u.c. (141); note that corresp. diethylene glycol *mono*trityl ether has m.p. 112.5–113.5° u.c. (141).]

[C̄ (2 moles) with triethylene glycol (1:6538) in pyridine gives (45–60% yield (141)) triethylene glycol ditrityl ether, m.p. 142.0–142.5° u.c. (141); note that this prod. is dimorphous, and an unstable form, m.p. 130.5–131.5° u.c., sometimes obtd. can be converted to the stable higher-melting form by htg. at 125° or by grinding in acetone (141).]

[C̄ with glycerol (1:6540) may give mono-, di-, or tritrityl ethers acc. to conditions; glycerol α-monotrityl ether, m.p. 93–94° (147), 92–94° (140), but also sometimes in another form of m.p. 108–110° (147) (148), 109–110° (149); glycerol α,α′-ditrityl ether, m.p. 174–177° (150), 174–176° cor. (151), 170–171° (140); glycerol α,α′,β-*tris*-trityl ether, m.p. 196–197° (147) (150). — Note that the relationships of these three ethers are subtle; e.g., the monoether at 180–190° is converted (147) into the α,α′-diether; the latter in turn at 260° gives (147) the triether.]

[C̄ (4 moles) with pentaerythritol (1:5850) in pyridine gives (145) a tetratrityl ether m.p. above 350°.]

With carbohydrates and their relatives. C̄ has recently been much employed as a tritylating agent for compounds of the carbohydrate group. This use started from the original (erroneous) impression that C̄ etherified hydroxyl groups only if the latter were primary. However, although C̄ does in general react preferentially with such primary hydroxyls, and this reaction has been proposed (155) as a means for the detection of primary alcs. in the presence of secondary and/or tertiary alcohols, yet such primary tritylation is *not* specific. Abundant evidence is already available (156) (157) (158) (159) that secondary hydroxyl groups undergo tritylation. Although the scope of this book cannot be extended to a detailed treatment of the use of C̄ as tritylating agent in the carbohydrate group, yet a few brief citations may be of service as leading references.

With various tetrahydric alcohols. [For behavior of C̄ with *meso*-erythritol (1:5825) and pentaerythritol (1:5850) see (145).]

With various pentahydric alcohols and pentoses. [For behavior of C̄ with adonitol, arabitol, xylitol, fucitol, rhamnitol, and epirhamnitol see (145); with arabinose, ribose, and xylose see (160); with various derivatives of these see (158) (167) (168).]

With various hexahydric alcohols and hexoses. [For behavior of C̄ with mannitol (145) (161), sorbitol (145), dulcitol (162) see indic. refs; with *d*-glucose (163) (164) (165), with *d*-galactose (165), with fructose (160) (166); with various derivs. of these see (159) (169) (152) (170) (171) (172) (173).]

With various disaccharides. [For behavior of C̄ with sucrose (174), maltose (174), turanose (175) see indic. refs.]

With various polysaccharides. [For behavior of C̄ with raffinose (174), glycogen (176), starch (177), cellulose (177), and arabogalactan (178) see indic. refs.]

With thiols (for thiophenols see below). C̄ with mercaptans yields the corresp. trityl thioethers [e g, C̄ with MeSH in dry ether or C_6H_6 gives (179) (180) trityl methyl sulfide [Beil. VI₁-(352)], lfts. from MeOH, m.p. 105° (179); C̄ with EtSH similarly gives (179) (180) trityl ethyl sulfide [Beil. VI₁-(353)], m.p. 125° (179). — C̄ with Na triphenylthiocarbinolate in alc. on htg. gives (95) ditrityl sulfide, m.p. 182° dec. (also obtd. from C̄ + abs. alc. Na_2S) — For tritylation with C̄ of SH groups in mercaptoacetic acid, α-mercaptopropionic acid (thiolactic acid), β-mercaptopropionic acid (thiohydracrylic acid, α-mercaptosuccinic acid (thiomalic acid) see (180)].

With phenols. C̄ with phenols (as with alcohols) gives in general the corresp. trityl ethers; however, with phenols there is a further complication in that [illegible] of the trityl radical of the ether or [illegible]

[illegible] [C̄ with KOC_6H_5 (89) (181) cf. (182) or $NaOC_6H_5$ (139) (182) in dry ether gives (yields: 90% (139), 71% (181), 70% (182)) trityl phenyl ether (α-phenoxytriphenylmethane) [Beil. VI-716, VI₁-(350)], m.p. 103° (89) (165) [illegible] accompanied by some *p*-tritylphenol [illegible] (364)], m.p. 282° (182), 280° (179); note [illegible] may represent as much as 74% yield [illegible] the former by use of "Claisen's alkali" (182), was originally (89) overlooked; note, also, that C̄ with phenol (1:1420) in pyridine at 100° for 3½ hrs. gave 28% yield (165) trityl phenyl ether, while C̄ with phenol at 130–140° for 4 hrs. gave (182) cf. (179) only 1 5% of this product and 98 5% of the isomeric *p*-tritylphenol.]

With the 3 cresols. [C̄ with *o*-cresol (1:1400) in pyridine at 110° for 5–6 hrs (183) (181) (184) or C̄ with sodium *o*-cresolate in dry [illegible] ls: 31–53% (183) [illegible] by as much as 26 [illegible], m p. 186° (185), [illegible] C̄ with sodium *o*-cresolate in excess *o*-cresol [illegible] hrs. (183) or C̄ with *o*-cresol at 180° for 5 hrs. (181) or in pres. of $ZnCl_2$ at 180° for ½ hr. (181) gives (33% yield (183)) 4-trityl-2-methylphenol — Note that this latter cryptophenol was originally (181) [illegible] the structure α- [illegible] since (186) (187) [illegible]

[C̄ with th [illegible] (53% yield (185)) [illegible] expected nuclear tritylation prod., viz , 4 [illegible] the latter has subsequently [illegible] (190), 213° (186)]

[illegible] at 100° for 7 hrs. (181) or 5 hrs. (191) (26) or C̄ with sodium *p*-cresolate in dry ether refluxed 2 hrs. (185) gives (yields: 80% (191), 50–60% (185)) trityl *p*-tolyl ether, the latter being definitely trimorphous and occurring in three forms; viz., m.p. 114° (185), 113–114° (191) (192) (26); m p 95° (193) (194); and m p. 81° (181) (193) (194) (note that the lower-melting forms tend to convert to the 114°

type (194)) accompanied by a trace of a cryptophenol, presumably 2-trityl-4-methylphenol, m.p. 182° (185) (190), also obtd. (64% yield (190)) from C̄ with sodium *p*-cresolate in excess *p*-cresol at 130–140° for 3 hrs.]

With other phenols. [For further examples of nuclear tritylation of phenols by use of C̄ with isochavibetol and isoeugenol see (196) cf. (26); with 2-hydroxynaphthoquinone-1,4 see (197). — *For formn. of di-trityl ethers from* pyrocatechol (1:1520) (140) or from hydroquinone (1:1590) (198) see indic. refs.]

With thiophenols. C̄ with thiophenol on htg. (199) or in C_6H_6 soln. on refluxing ½ hr. (180) (179), or C̄ with $NaSC_6H_5$ in ether at ord. temp. for 18 hrs. (200) (201), gives (yield alm. quant. (199) (200), 96% (180)) trityl phenyl sulfide, m.p. 106.5° (180), 106° (201), 105–106° (199) (200), 105° (179); this prod. on oxidn. with $CrO_3/AcOH$ gives (199) the corresp. sulfoxide, m.p. 163°, but is unaffected by H_2O_2 (199) [for corresp. sulfone, m p. 175–176° (210), see below under reaction of C̄ with salts of organic acids (sodium benzenesulfinate)].

[For corresp. sulfides from C̄ with *o*-thiocresol, *p*-thiocresol, α-thionaphthol, β-thionaphthol, 2,4-dinitrothiophenol see (201).]

With enols or enolates. [For examples of reaction of C̄ with the enol form of diphenylacetaldehyde (202), methyl diphenylacetate (202), or with stilbenediol *bis*-MgI cpd. (203) see indic. refs.]

Behavior of C̄ with Ethers

C̄ with various aliphatic ethers in the pres. of suitable catalysts yields triphenylmethane and an aldehyde [e.g., C̄ with diethyl ether in the pres. of $AlCl_3$ (56) (77), $FeCl_3$ (65), or $ZnCl_2$ (78) gives triphenylmethane and acetaldehyde; although the latter is lost by polymerization the method is standard (77) for prepn. of triphenylmethane (1:7220)].

[Note, however, that with aromatic ethers nuclear tritylation occurs: e.g., C̄ with anisole (1:7445) + $SnCl_4$ at 100–110° for 1 hr. gives (45% yield (204)) 4-tritylanisole, m.p. 200.5° (204)]

Behavior of C̄ with Organic Acids

(For salts of organic acids see below.)

C̄ with AcOH even at 13° (133) (146) cf. (50) is in equilibrium with trityl acetate (see below) + HCl. — C̄ with thiolacetic acid (CH_3COSH) gives trityl thiolacetate [Beil. VI-721, VI_1-(353)], m.p 138° (179). — C̄ with thiolbenzoic acid (C_6H_5COSH) in toluene gives (85% yield (180)) trityl thiolbenzoate [Beil. IX-422, IX_1-(170)], m.p. 187.5–188° (180). — C̄ with free thiocyanic acid in C_6H_6 gives (97% yield (180)) trityl thiocyanate, m.p. 139° (180) (see also below).

Behavior of C̄ with Salts of Organic Acids

C̄ with salts of organic acids normally reacts to yield the corresp. trityl esters.

C̄ with AgOAc in dry ether or C_6H_6 on shaking at room temp. (57) or in C_6H_6 refluxed 2 hrs. (46), or C̄ shaken with NH_4OAc in C_6H_6 at ord. temp. (205), gives trityl acetate, cryst. from AcOEt + lgr., m.p. 87–88° (46) (57). — C̄ with AgOBz in C_6H_6 at 60° for 4 hrs. gives (96) trityl benzoate, m.p. 165–166° (96). — Note that in analogous fashion C̄ might be expected to react with silver salts of *p*-nitrobenzoic and 3,5-dinitrobenzoic acids to give corresp. esters, but these are unreported.

[C̄ with excess dry Ag_2CO_3 in dry C_6H_6 shaken 24 hrs. gives (60–80% yield (106)) (105) ditrityl carbonate, cryst. from xylene, m.p. 209° dec. (106), 205–210° (105); this prod. on htg. in xylene in pres. of Cu pdr. decomposes (106) (105) into CO_2 and ditrityl ether, m p. 237–238° (106) (see also above under C̄ with HgO).]

[C̄ with excess $Hg(CN)_2$ at 150–170° for 1 hr. gives (alm. 100% yield (53)) on extraction

with C_6H_6 (53) (206) (207) trityl cyanide (triphenylacetonitrile) [Beil. IX-714, IX_1-(309)], pr. from AcOH, m.p. 129° (208), 127.5° (53).]

[C̄ with mercury fulminate in dry C_6H_6 under cooling gives (65% yield (208)) trityl cyanide oxide, $(C_6H_5)_3CNO$, ndls. from alc., m.p. 153–154° (208).]

[C̄ with KSCN in dry C_6H_6 shaken at room temp. for 2 days gives (209) trityl thiocyanate [Beil. VI-721], m.p. 137° (209) (see also above under C̄ with organic acids (HSCN)).]

[C̄ with sodium benzenesulfinate in dry ether gives (210) trityl phenyl sulfone [Beil. VI-721], lfts. from ether, m.p. 175–176° (210); note that corresp. sulfoxide (see above under behavior of C̄ with thiophenol) has m.p. 163°. — Similarly, C̄ with sodium p-toluenesulfinate in dry C_6H_6 gives (179) trityl p-tolyl sulfone [Beil. VI_1-(353)], m.p. 173° (179).]

Behavior of C̄ with Organometallic Compounds

This topic cannot be fully expanded within the scope of this book, but the following examples will serve as leading references.

With organo-alkali compounds. [C̄ with Li n-butyl in pet. ether for 9 days gives (26% yield (211)) 1,1,1-triphenylpentane, m.p. 153–154° (211). — C̄ with Li C_6H_5 gives (212) free trityl isolated in form of (20% yield) ditrityl peroxide.]

[C̄ with Na n-butyl or Na trityl in liq. NH_3 + toluene (112) or C̄ with Na trityl in dry ether (108) gives free trityl. — C̄ with Na + tetraphenylethylene as directed gives (213) pentaphenylethyl.]

With RMgX compounds. C̄ with MeMgBr (214) or C̄ with MeMgI (215) gives no gas (216) cf. (217) (218) but couples giving (yields: 95% (214), 70% (215)) 1,1,1-triphenylethane (α-methyltriphenylmethane) [Beil. V-709, V_1-(350)], cryst. from alc., m.p. 94–95° (214) (215), 94.8–95.0° (15); note that this prod. is also obtd. from MeMgBr with trityl acetate (61% yield (219)) or from K trityl with MeI in liq. NH_3 (85–94% yield (220)).

[C̄ with EtMgBr in dry ether reacts rapidly and quant. (221) yielding (215) not only the expected 1,1,1-triphenylpropane [Beil. V-712], m.p. 51° (215), but also (215) triphenylmethane (1:7220) and ethylene.]

[C̄ with n-PrMgBr in dry ether gives (215) not only 1,1,1-triphenylbutane, m.p. 79° (215), but also considerable triphenylmethane (1:7220). — C̄ with iso-PrMgBr in dry ether gives (215) not only 1,1,1-triphenyl-2-methylpropane, b.p. 233–234° at 21 mm. (215), but also much triphenylmethane (1:7220).]

[C̄ with C_6H_5MgBr in dry ether or C_6H_6 gives a small yield (25–30% (222), 10–12% (139), 5–10% (215) (223)) tetraphenylmethane [Beil. V-738, V_1-(371), V_2-(672)], m.p. 281–282° (224) (225), b.p. 431° at 760 mm. (225), but the principal product (yield: 50–77% (222), 47.4% (226)) is 4-benzohydrylbiphenyl (p-phenyltetraphenylmethane) [Beil. V-738, V_2-(672)], m.p. 111° (226), 112–113° (116); for explanation and study of this reaction see (222). — Note that C̄ with C_6H_5MgI behaves differently giving (227) cf. (179) triphenylmethyl and biphenyl (1:7175).]

[C̄ in C_6H_6 with benzyl MgCl in dry ether gives (100% yield (215)) (228) 1,1,1,2-tetraphenylethane [Beil. V-740, V_1-(372), V_2-(674)], m.p. 144° (215), 143.5–143.7° (15). — C̄ with benzohydryl bromide + Mg in dry ether (215) cf. (230) (or better trityl MgBr + benzohydryl bromide (229) cf. (230)) gives (90% yield (229)) pentaphenylethane [Beil. V-755, V_1-(386), V_2-(711)], m.p. in air 166–178° (229), in N_2 182–185° (229). — C̄ with trityl MgCl gives (230) free trityl.]

[For behavior of C̄ with phenylacetylenyl MgBr giving trityl-phenylacetylene or with acetylene-*bis*-MgBr giving di-tritylacetylene (hexaphenylbutyne-2) see (231).]

Behavior of $\bar{C}$ with (Organic) Amines

(For $\bar{C}$ with NH_3, NH_2OH, NH_2NH_2, etc., see above under $\bar{C}$ with inorganic nitrogen compds; for $\bar{C}$ with arylhydrazines see below.)

$\bar{C}$ with Primary Amines

[$\bar{C}$ with $MeNH_2$ in C_6H_6 in pres. of NaOMe gives (125) trityl-*N*-methylamine [Beil. XII-1344, XII_1-(557)], m.p. 73° (125) (236) (corresp. $\bar{B}$.HCl, m.p. 216° (125)).]

With aromatic *prim.* amines. $\bar{C}$ in C_6H_6 with aniline in alc. refluxed 15 min. gives (80% yield (228)) (57) *N*-tritylaniline [Beil. XII-1344, XII_1-(557)], cryst. from alc / ether, m.p. 149–150°, (57), 148–149° (237), 146° (228) [note that this prod. with ½ its wt. $ZnCl_2$ at 160° for 15 min. rearranges (228) to *p*-tritylaniline [Beil. XII-1348], ndls. from toluene or alc., m.p. 256° cor. (225), 249° (228); note also that $\bar{C}$ is claimed to form with aniline an addn. cpd., m.p. 189–190° (34)].

[$\bar{C}$ in C_6H_6 with *o-toluidine* in alc. refluxed 15 min. gives (228) *N*-trityl-*o*-toluidine, m.p. 142.5° (228), 142° (237) (238), 140–142° (57); this prod. with $ZnCl_2$ at 160° for 15 min. rearranges (82% yield (189)) (228) to 4-trityl-2-methylaniline, m.p. 216° (228), 215° (189) (*not* to α-(2-amino)-β,β,β-triphenylethane as originally supposed (228) cf. (189)). — $\bar{C}$ with *m-toluidine* directly has not been studied nor has the other expected product, viz., *N*-trityl-*m*-toluidine, nor its rearr. prod., been reported. — $\bar{C}$ in C_6H_6 with *p-toluidine* in alc. refluxed 15 min. gives (228) *N*-trityl-*p*-toluidine [Beil. XII-1344], m.p. 180° (228), 177–178° (85), 177° (238), 176° (237): this product with $ZnCl_2$ at 190° for 30 min. does *not* (228) rearrange.]

[$\bar{C}$ with *p*-aminobiphenyl (*p*-xenylamine) in C_6H_6 on htg. gives (82% yield (239)) *N*-trityl-*p*-xenylamine, pr. from C_6H_6, m.p. 179.5–180.5° (239); note that this prod. does *not* rearrange.]

$\bar{C}$ with Secondary Amines

With aliphatic *sec.* amines. [$\bar{C}$ with Me_2NH in C_6H_6 gives (65% yield (240)) trityldimethyl-amine, cryst. from abs. alc., m.p. 95–97° (240), 97° (236).]

With aromatic *sec.* amines. [$\bar{C}$ with diphenylamine might first be expected to give *N*-trityl-diphenylamine, ndls. from toluene, m.p. 172° (241), which has actually been prepd. by other means (241) (242) (243); however, $\bar{C}$ with diphenylamine (244) in hot C_6H_6 (243) or pyridine (165) or the above *N*-trityl-diphenylamine with diphenylamine HCl in C_6H_6 or in hot AcOH directly (243) gives the rearr. prod., viz., 4-trityl-diphenylamine (4-anilinotetraphenylmethane), m.p. 242° (243) (244), 240° (165). — For use of these and related prods. as antioxidants see (244) (245). —For analogous behavior of $\bar{C}$ with di-*p*-tolylamine, di-*p*-amylamine, and di-(*p*-dimethylaminophenyl)amine see (243).]

[For behavior of $\bar{C}$ with *N,N*-diphenyl-*p*-phenylenediamine yielding a blue meriquinoid salt, m.p. 182–183°, see (246) (247) (248); with indole and with 2-methylindole giving *N*-trityl derivs. see (196).]

With heterocyclic *sec.* amines. [$\bar{C}$ with piperidine in C_6H_6 yields (179) *N*-tritylpiperidine, ndls. from alc., m.p. 153° (179).]

$\bar{C}$ with Tertiary Amines

With aliphatic *ter*-amines. [$\bar{C}$ with Me_3N in acetonitrile + $CHCl_3$ at room temp. ppts. a prod., m.p. 190–195° dec. (249), of compn. $2(C_6H_5)_3COH.(CH_3)_3$ N.HCl from which extraction with aq. leaves triphenylcarbinol (1:5985), m.p. 161°, or from which extraction with C_6H_6 leaves the trimethylamine HCl. — For analogous behavior of $\bar{C}$ with Et_3N see (249)]

With aromatic *ter*-amines. [$\bar{C}$ with 3 wts. dimethylaniline at 100–115° for 8 hrs. gives (42% yield (250)) 4-trityldimethylaniline (4-dimethylamino-tetraphenylmethane), cryst. from alc., m.p. 204–205° (250), 208° (251).]

With heterocyclic *ter*-amines. [$\bar{C}$ with pyridine does not give a simple quaternary salt; however, $\bar{C}$ with pyridine in nitromethane + $CHCl_3$ (249) or in EtOAc (249), or $\bar{C}$ in dry pyridine with exactly 1 mole H_2O (84) (252) (165), gives a definite prod., cryst. from acetone (249) or $CHCl_3$ (42), m.p. 176° (42), 174° (34) (253) (165), 172–174° (84), 170–175° (249); this prod. is formulated as either $(C_6H_5)_3C.OH.C_5H_5N.HCl$ (249) or as $(C_6H_5)_3CCl.C_5H_5N.H_2O$ (84) (252) (42).]

Behavior of $\bar{C}$ with Arylhydrazines

With monoarylhydrazines. $\bar{C}$ with phenylhydrazine (2 moles) in dry ether at room temp. gives (90% yield (254)) *N*-trityl-*N*-phenylhydrazine [Beil. XV-581, XV_1-(184)], cryst. from boilg. abs. alc., m.p. 136–137° (254), 148° (255). [Note that this prod. is easily oxidized (dehydrogenated), e.g., with nitrous oxides (100% yield (254), 86% (256)) or Br_2/aq. (100% yield (257)) giving tritylazobenzene $(C_6H_5)_3C—N{=}N—C_6H_5$ [Beil. XVI-85], m.p. 113–114° (254), 110° (255), 110–112° (256) (for study of thermal decompn. of this prod. see (258)).]

[$\bar{C}$ with *p*-nitrophenylhydrazine in a large vol. C_6H_6 gives (257) cf. (256) *N*-trityl-*N*-(*p*-nitrophenyl)hydrazine, m.p. 170° (250).]

With diarylhydrazines. [$\bar{C}$ with *N,N*-(*unsym.*)-diphenylhydrazine (2 moles) in C_6H_6 refluxed 20 min. gives (259) *N'*-trityl-*N,N*-diphenylhydrazine, m.p. 136–137° (259). — $\bar{C}$ with *N,N'*-diphenylhydrazine (hydrazobenzene) (2 moles) in dry ether under CO_2 refluxed 16 hrs. gives (259) *N'*-trityl-*N,N*-diphenylhydrazine, m.p. 107° (259) (in this connection recall also that $\bar{C}$ with hydrazobenzene in boilg. C_6H_6 is in part reduced (79) to triphenylmethane).]

Behavior of $\bar{C}$ with Amides

[$\bar{C}$ (2 moles) with urea (1 mole) in dry pyridine at 100° gives (165) cf. (179) *N,N'*-ditritylurea, cryst. from alc. with 2 EtOH not lost on air drying, m.p. 245° (165); note that *N*-tritylurea (prepd. indirectly (124)) has m.p. 234–235° dec. (124). — $\bar{C}$ (1 mole) + thiourea in pyridine at 100° for 1 hr. gives (165) cf. (179) *N*-tritylthiourea, cryst. from C_6H_6, m.p. 222° dec. (165), 217° (179).]

Behavior of $\bar{C}$ with Hydrazides

[$\bar{C}$ with free semicarbazide ($NH_2CONH.NH_2$) in pyridine at 0° gives (88% yield (260)) 1-tritylsemicarbazide, cryst. from abs. alc. with 1 EtOH, m.p. 186–188° dec.; the solvate alc. is lost in vac. at 110° after 6 hrs. and m.p. rises to 190–192° (260).]

[$\bar{C}$ with primary hydrazides (acylhydrazine) in general reacts to give *N*-trityl-*N*-acylhydrazines which upon suitable dehydrogenation give *N*-trityl-*N*-acyl-azo compounds; the topic cannot here be expanded but for many examples see (260) (261).]

- Ⓓ Triphenylmethane (1:7220): lfts. from alc. [From $\bar{C}$ in anhydrous formic acid (1:1005) at 100° for 2 hrs. in 90% yield (4).]
- Ⓓ Triphenylcarbinol (1:5985): cryst. from C_6H_6 or alc., m.p. 161–162°. [From $\bar{C}$ on boilg. with aq.]
- Ⓓ Trityl methyl ether: cryst. from MeOH, m.p. 82–83°. (See text above under behavior of $\bar{C}$ with alcohols.)
- Ⓓ Trityl ethyl ether: cryst. from EtOH, m.p. 83–84°. (See text above under behavior of $\bar{C}$ with alcohols.)

Ⓓ *N*-Tritylphthalimide: tbls. from alc., m.p. 172° (179). [From C̄ with K phthalimide at 200° (179).]

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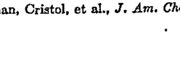
3:3415 3,4′-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ **Beil. S.N. 652**
(*m*-Chlorophenyl *p*-chlorophenyl ketone)



M.P. 112.6–113.4° (1)

[For prepn. of C̄ from 1,1-dichloro-2-(*m*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene (3:9863) by oxidn. with CrO_3 (41% yield) see (1).]

Ⓓ **3,4′-Dichlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 258–260° (1).

3:3415 (1) Haller, Bartlett, Drake, Newman, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1601–1602 (1945).

3:3420 5,8-DICHLORONAPHTHOL-1

$C_{10}H_6OCl_2$

Beil. VI - 613
VI_1—
VI_2—

M.P. 114–115° (1)

Cryst. (from CS_2) (1). — Spar. sol. hot aq. (1).

[For prepn. (in very poor yield) from γ-(2,5-dichlorophenyl)paraconic ac. [Beil. XVIII-422] by distn. see (1).]

$\bar{C}$ with $FeCl_3$ gives a white turbidity, changing on warming to flocculent violet ppt. (1).

$\bar{C}$ in alk. soln. coupled with diazotized naphthionic acid (1-naphthylaminesulfonic acid-4) gives dark violet color (1).

[For use in dyestuff industry see (2) (3) (4).]

Ⓓ 5,8-Dichloro-1-naphthyl acetate: yellowish pr. from CS_2 + lgr., m.p. 144–145° (1).

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3:3432 CHLOROMALEIC ACID

Cl—C—COOH
‖
H—C—COOH

$C_4H_3O_4Cl$

Beil. II - 752
II_1—
II_2-(646)

M.P. 115°	(1) (2)
114–115°	(3) (4)
[108° after sintering at 95° (5) (6)]	

[*See also chlorofumaric acid* (3:4853).]

Cryst. from AcOH/$CHCl_3$, ether/$CHCl_3$, ether/pet. ether, or ether alone. — Eas. sol. alc, ether, AcOH; spar. sol $CHCl_3$ or C_6H_6; insol. pet. ether.

[For prepn. of $\bar{C}$ from *meso*-α,α'-dichlorosuccinic acid (3:4930) with NaOAc/dil. AcOH on boilg. (5) (1), or from its neutral sodium salt in aq soln. on boilg ½ hr. (4), see indic. refs; from chloromaleic anhydride (3:0280) by hydrolysis with aq. and subsequent evapn. see (4) (5) (6) (7); from 3,5,5,5-tetrachloro-4-ketopenten-2-oic acid-1 ("β-(trichloroacetyl)-β-chloroacrylic acid") [Beil. III-733] on 24 hr. stdg. at room temp. of its soln. in excess 10% aq Na_2CO_3 see (6); from chloromaleonitrile (b.p 185° at 753 mm., 71.0–71.5° at 10 mm., D_4^{20} = 1.2293, n_D^{20} = 1.48944 (9)) by hydrol see (9).]

$\bar{C}$ on htg. at 180° loses H_2O yielding (6) chloromaleic anhydride (3:0280).

$\bar{C}$ although unchanged by conc. HCl at ord. temp. for as long as 10 days (4) is by repeated evapn with conc HCl (7) isomerized to chlorofumaric acid (3:4853).

$\bar{C}$ in aq soln with Zn filings is dehalogenated yielding (4) fumaric acid (1:0895); $\bar{C}$ (as $Na_2\bar{A}$) in aq soln with 1% Na/Hg gives (4) mainly succinic acid (1:0530) accompanied by some fumaric acid (1:0895).

$\bar{C}$ readily reduces aq. $KMnO_4$.

[$\bar{C}$ readily combines with Br_2 if heated in s.t. to 100° (7).]

$\bar{C}$ behaves normally as a dibasic acid: e g, titration with standard dil. aq. alk. gives Neut. Eq 75 3; for study of electrometric titration see (1).

[*Salts:* $KH\bar{A}$, eas. sol. aq (dif. from corresp salt of chlorofumaric acid (3:4853)), e.g., 100 g. of its satd. aq soln at 15° cont. 29.2 g of $KH\bar{A}$ (7); for crystallographic data see (7).

— $NaH\bar{A}.3H_2O$, eas. sol. aq. (7). — $Ag_2\bar{A}$, insol. aq. (7). — $Ba\bar{A}.2H_2O$ (4) (5) (6), spar. sol. aq. — $Ca\bar{A}.4H_2O$ (4). — $Sr\bar{A}.4\frac{1}{2}H_2O$, spar. sol. cold aq. (5). — $Pb\bar{A}$, insol. aq. (4).]

[$\bar{C}$ on stdg. at ord. temp. with slight excess 0.76 N aq. KOH gives chlorine ion only $\frac{1}{40}$ as rapidly (4) as the isomeric chlorofumaric acid (3:4853).]

The acid chloride corresp. to $\bar{C}$, viz., chloromaleyl (di)chloride (3:6158) q.v., has been reported only by indirect means.

—— Dimethyl chloromaleate: oil (see 3:9351).

—— Diethyl chloromaleate: oil (see 3:6697).

Ⓓ Chloromaleanil [N-phenyl-chloromaleimide]: ndls. from boilg. alc., m.p. 170° (8). [From aniline salt of $\bar{C}$ (or of chlorofumaric acid) on htg. for a few minutes at 170–180° (8); note that this prod. on htg. with aniline yields (8) α-anilinosuccinanil [Beil. XXI-554, XXI_1-(432)], yel. cryst. from acetone + C_6H_6, m.p. 232° (8), and that a little of this latter cpd. which may accompany the former is readily removed from it by washing with warm C_6H_6 (8).]

Ⓓ Chloromaleic p-chloroanil [N-(p-chlorophenyl)chloromaleinimide]: pl. from hot alc., m.p. 175° (8). [From p-chloroaniline salt of $\bar{C}$ on htg. for a few minutes at 170–180° (8).]

Ⓓ Chloromaleic p-bromoanil [N-(p-bromophenyl)chloromaleinimide]: microcrystn. powder from boilg. alc., m.p. 190° (8). [From p-bromoaniline salt of $\bar{C}$ on htg. for a few minutes at 170–180° (8).]

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3:3445 2,7-DICHLORONAPHTHALENE

$C_{10}H_6Cl_2$ Beil. V - 544
V_1—
V_2-(446)

M.P. **115°** (10)
114–115° u.c. (1)
114° (2) (3)

Cryst. from alc. or C_6H_6; sublimes under reduced press. — Eas. sol. boilg. alc.

[For prepn. of $\bar{C}$ from naphthalene-2,7-*bis*-(sulfonyl chloride) [Beil. XI-217] (4) (1), from 7-chloronaphthalene-2-sulfonyl chloride [Beil. XI-181] (4) (5), from 7-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (7), from sodium 7-hydroxynaphthalenesulfonate-2 [Beil. XI-285, XI_1-(67)] (3) by htg. with PCl_5 as directed, see indic. refs.; from 7-sulfonaphthylamine-2 [Beil. XIV-763, XIV_1-(736)] by treatment of the corresp. *diazonium* chloride with PCl_5 in $POCl_3$ see (8); from 3,6-dichloronaphthalimide or 3,6-dichloronaphthalic acid (3:4870) with HgO + aq. in s.t. 6 hrs. at 200–210° see (10).]

$\bar{C}$ on oxidn. with dil. HNO_3 (D = 1.21) in s.t. at 140° yields (9) 4-chlorophthalic acid (3:4390), m.p. 157°.

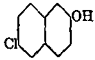
[$\bar{C}$ on mononitration yields (9) a prod., m.p. 141.5–142°.]

[$\bar{C}$ on treatment with chlorosulfonic acid in CS_2, followed by conversion as directed (11), yields mixt. of two sulfonic acids; the major prod. is 2,7-dichloronaphthalenesulfonic acid-3 (corresp. sulfonyl chloride, m.p. 166°, corresp. sulfonamide, m.p. 218° (12)), the minor prod. (10% of total) is 2,7-dichloronaphthalenesulfonic acid-4 (corresp. sulfonyl chloride, m.p. 152°) (11).]

CHAPTER IX

VISION A. SOLIDS

(3:3500-3:3999)

-2  $C_{10}H_7OCl$ Beil. VI - 649
VI₁—
VI₂-(603)

., ether, AcOH, C_6H_6, $CHCl_3$, CS_2 — Sublimes in
naphthol-2 (3:2965), m p 101° to 79–88° (2).
phthol-2 (3:3600) with $FeSO_4$ + NaOH see (4);
'2) (3) with Na/Hg in dil. HCl see (2) (3); from K
XI-282, XI₁-(66)] with 3 moles PCl_5 at 165° as

press and at elevated temp. yields (5) 6-chloro-
AcOH, m.p. 260° (5)]
) in s t. at 190–200° gives (6) 4-chlorophthalic

'4–125° (3).
ndls. from much alc., m.p. 146–147° (2).
nd shaken with *m*-nitrobenzoyl chloride (2).]

5 (1881) (2) B...

C_8H_9OCl Beil. VI —
VI₁—
VI₂-(463)

I_3

:nol = *sym.-m*-xylenol)')
6% yield (2)) or from
Cl_2 or SO_2Cl_2 (5) see
) (3:0844
compl

from pentachlorobenzene (3:2290) with $N/2$ MeOH/NaOMe at 180° in *s.t. for* 7½ hrs. (note that some of the iosmeric 2,3,4,5-tetrachlorophenol (3:3523) is also formed) see (1).]

C̄ in aq. behaves as a fairly strong acid, K at 25° = 3.3×10^{-6} (2), and can be directly titrated with $N/10$ aq. NaOH (3) (1), Neut. Eq. = 232.

C̄ (1 wt. pt.) added to HNO_3 (D = 1.5, 6 wt. pts.) in 20 pts. AcOH at 10°, and after 1 hr. poured onto ice, gives (65% yield (4)), 2,3,5,6-tetrachloro-4-nitrophenol, ndls. from AcOH, m.p. 148–149° dec. (4) (corresp. acetate, ndls. from dil. alc., m.p. 113–114° (4)).

Ⓓ **2,3,5,6-Tetrachlorophenol methyl ether (2,3,5,6-tetrachloroanisole):** ndls. from alc., m.p. 88° (1). [From C̄ with alk. + Me_2SO_4 (1).] — [Note that this prod. on nitration with 4–5 wt pts. HNO_3 (D = 1.5) at 0° gives (95% yield (4)) 2,3,5,6-tetrachloro-4-nitroanisole, ndls. from dil. alc., m.p. 112–113° (4).]

—— **2,3,5,6-Tetrachlorophenol ethyl ether (2,3,5,6-tetrachlorophenetole):** m.p. 56° (5). [Reported by indirect means (5).]

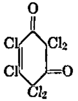
—— **2,3,5,6-Tetrachlorophenyl acetate:** unreported.

Ⓓ **2,3,5,6-Tetrachlorophenyl benzoate:** m.p. 136° (5). [From C̄ + large excess BzCl in aq. alk. (5).]

—— **2,3,5,6-Tetrachlorophenyl *N*-phenyl carbamate:** unreported.

3:3460 (1) Holleman, van der Hoeven, *Rec. trav. chim.* **39**, 746–748 (1920). (2) Tiessens, *Rec trav. chim.* **48**, 1068 (1929). (3) Tiessens, *Rec. trav. chim.* **50**, 116, 119 (1931). (4) Peters, Rowe, Stead, *J. Chem. Soc.* **1943**, 233–235. (5) Bures, Kovarovicova, *Časopis Českoslov. Lékárnictva* **10**, 197–202, 233–239 (1930); *Cent.* **1930**, II 2775; *C.A.* **25**, 1816–1817 (1931).

3:3470 1,2,4,4,6,6-HEXACHLORO-CYCLOHEXEN-1-DIONE-3,5 ("Hexachlororesorcinol") $C_6O_2Cl_6$ Beil. VII - 572, VII₁—



M.P. 115° (1) B.P. 159–160° at 13–15 mm. (1)

Colorless tbls. or thick pr. (from AcOH or ether/pet. ether). — Penetrating lachrymatory odor. — *C̄ can be distd at atm. press. without decompn. — Eas. sol. ether, $CHCl_3$, C_6H_6;* spar. sol. pet. ether. — Readily forms supersatd. solns.

[Fc ... by actn. of Cl_2 in AcOH see (1).]

C̄ ... AcOH reduces smoothly (1) to tetra

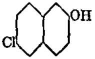
[For use as seed disinfectant see (2); for other reactions see (1).]

3:3470 (1) Zincke, Fuchs, *Ber.* **24**, 2689–2690 (1892). (2) Bonrath, Urbschat (to I.G.), Ger. 534,597, Sept. 29, 1931, *Cent.* **1931**, II 3143.

CHAPTER IX

DIVISION A. SOLIDS

(3:3500–3:3999)

3:3500 6-CHLORONAPHTHOL-2  $C_{10}H_7OCl$ Beil. VI - 649
VI$_1$—
VI$_2$-(603)

M.P. 115° (1) (2) (3) (4)

Ndls. from hot aq. (1) (2); sol. alc., ether, AcOH, C_6H_6, $CHCl_3$, CS_2. — Sublimes in prisms. — $\bar{C}$ depresses m p of 8-chloronaphthol-2 (3:2965), m.p. 101° to 79–88° (2).

[For prepn of $\bar{C}$ from 1,6-dichloronaphthol-2 (3:3600) with $FeSO_4$ + NaOH see (4); from 6-chloronaphthol-2-sulfonic acid-4 (2) (3) with Na/Hg in dil HCl see (2) (3); from K salt of 2-naphtholsulfonic acid-6 [Beil. XI-282, XI$_1$-(66)] with 3 moles PCl_5 at 165° as directed see (1) (2).]

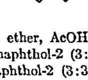
[$\bar{C}$ (as dry sodium salt) with CO_2 under press. and at elevated temp yields (5) 6-chloro-2-hydroxynaphthoic acid-3, yel. lfts. from AcOH, m.p. 260° (5).]

$\bar{C}$ on oxidn. with dil. HNO_3 (D = 1.13) in s.t. at 190–200° gives (6) 4-chlorophthalic acid (3:4390).

Ⓓ 6-Chloro-2-naphthyl benzoate: m.p. 124–125° (3).

Ⓓ 6-Chloro-2-naphthyl *m*-nitrobenzoate: ndls from much alc., m.p. 146–147° (2). [From $\bar{C}$ dislvd. in 10% NaOH at 50–60° and shaken with *m*-nitrobenzoyl chloride (2).]

3:3500 (1) Claus, Zimmermann, *Ber.* **14**, 1483–1485 (1881). (2) Ruggli, Knapp, Merz, Zimmermann, *Helv. Chim. Acta* **12**, 1048–1050 (1929). (3) Battegay, Silbermann, Kienzle, *Bull. soc. chim.* (4) **49**, 721 (1931) (4) Herzberg, Spengler, Schmid (to I.G.), Ger. 431,165, June 30, 1926; *Cent.* **1926**, II 1196 (5) Lange, Luce, Jacobs (to I.G.), Ger. 564,128, Nov. 14, 1932; *Cent.* **1933**, II 446. (6) Claus, Dehne, *Ber.* **15**, 321 (1882).

3:3505 4-CHLORO-3,5-DIMETHYLPHENOL (2-Chloro-*m*-5-xylenol)  C_8H_9OCl Beil. VI —
VI$_1$—
VI$_2$-(463)

M.P. 115–116° (1) **B.P. 246° (2)**
115° (3) (4)
114–115° (2)

Cryst. from benzene.

[For prepn of $\bar{C}$ from 3,5-dimethylphenol (*m*-5-xylenol = *sym*-*m*-xylenol) (1:1455) with SO_2Cl_2 (1 mole) in $CHCl_3$ (1) or with Cl_2 in AcOH (66% yield (2)) or from crude coal-tar fraction consisting mainly of 3,5-dimethylphenol with Cl_2 or SO_2Cl_2 (5) see indic. refs. (note that some 2-chloro-3,5-dimethylphenol (6-chloro-*m*-5-xylenol) (3:0844) is formed as a by-product (1) (5); also that 3,5-dimethylphenol in AcOH on complete saturation

[Note that, in addition to its ordinary use to designate $\bar{C}$ specifically, the term "chloralide" is also used generically to denote a class of compounds formed by condensation of chloral (3:5210) with α-hydroxy acids.]

Cryst. from alc. or ether; eas. sublimable; insol. aq.; eas. sol. hot but spar. sol. cold alc.; eas. sol. ether; eas. sol. in 80% AcOH (dif. and sepn. from metachloral (1)). — For crystallographic studies see (10).

Note that m.p. of $\bar{C}$ is almost identical with that of α-parachloral, m.p. 116°, but that mixed m.p. of the two is depressed as low as 85–90° (2); β-parachloral, however, has m.p. 152° (2).

[For prepn. of $\bar{C}$ from chloral (3:5210) or chloral hydrate (3:1270) with conc. or fumg. H_2SO_4 (yields: 61% (11), 44–51% (4) both based on chloral hydrate) see (11) (4) (8) (12) (6); for formn. of $\bar{C}$ from chloral hydrate with H_2SO_4 as a by-product (abt. 2% (2)) in prepn. of α- and β-parachloral + metachloral, or from chloral by warming with $AlCl_3$ (1), see indic. refs.; for formn. of $\bar{C}$ from chloral with $ClSO_3H$ as by-prod. of prepn. of octachlorodiethyl ether (3:0738) see (3); for formn. of $\bar{C}$ from chloral (excess) with β,β,β-trichloro-α-hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III_1-(111), III_2-(210)] in s.t. at 150–160° see (4) (13) cf. (17).]

[$\bar{C}$ on reduction with Zn + HCl in alc. soln. gives according to conditions very small amts. of β,β-dichloroacrylic acid (3:1875) (14) (15) (16), β-chloroacrylic acid (3:2240) (11), and acetaldehyde (1:0100) (15) (16).] — [$\bar{C}$ is unaffected by boilg. HNO_3 (8).]

[$\bar{C}$ with PCl_5 in s.t. at 270–290° for several days gives (18) (9) 5-chloro-2,5-*bis*-(trichloromethyl)dioxolane-1,3-one-4 ("trichlorolactic acid-tetrachloroethylidene ether-ester") [Beil. XIX-105], oil, b.p. 276° (18), D_4^{20} = 1.7426 (18).]

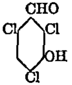
$\bar{C}$ with boilg. alkalies undergoes hydrolytic cleavage yielding (4) (12) (6) (7) chloroform (3:5050) and salts of formic acid (1:1005).

[$\bar{C}$ with abs. EtOH in s.t. at 140–150° gives (16) (4) chloral ethylalcoholate (3:0860) and ethyl β,β,β-trichlorolactate [Beil. III-287, III_1-(111), III_2-(210)], m.p. 66–67°.]

3:3510 (1) Böeseken, *Rec. trav. chim.* **29**, 108 (1910). (2) Chattaway, Kellett, *J. Chem. Soc.* **1928**, 2709–2712. (3) Fuchs, Katscher, *Ber.* **62**, 2384–2385 (1929). (4) Wallach, *Ann.* **193**, 4, 8, 11–19 (1878). (5) Wallach, *Ber.* **6**, 118, Note (1873). (6) Städeler, *Ann.* **61**, 104–114 (1847); **106**, 253–255 (1858). (7) Personne, *Bull. soc. chim.* (2) **21**, 529 (1874). (8) Grabowski, *Ber.* **8**, 1433–1437 (1875). (9) Anschütz, Haslam, *Ann.* **239**, 297–300 (1887). (10) Wallach, Bodewig, *Ann.* **193**, 58–59 (1878); *Z. Krist.* **1**, 594 (1877).

(11) Otto, *Ann.* **239**, 262–266 (1887). (12) Kekulé, *Ann.* **105**, 293–295 (1858). (13) Wallach, Heymer, *Ber.* **9**, 545–547 (1876). (14) Wallach, *Ann.* **203**, 83–84 (1880). (15) Wallach, *Ann.* **193**, 6, 20, 27 (1878). (16) Wallach, *Ber.* **8**, 1578–1583 (1875). (17) Routala, Neovius, *Ber.* **57**, 252, Note 4 (1924). (18) Anschütz, Haslam, *Ann.* **253**, 121–123 (1889).

3:3520 2,4,6-TRICHLORO-3-HYDROXYBENZALDEHYDE



$C_7H_3O_2Cl_3$ Beil. VIII-61, $VIII_1$—

M.P. 115.5–116.5° (1)
115–116° (6)
114° (2)
113° (3)

Colorless cryst. from 50% AcOH; $\bar{C}$ seps. with AcOH of crystn. but this immediately effervesces in air. — $\bar{C}$ has pronounced sternutatory props. and on moist skin produces painful blisters (2).

[For prepn. of $\bar{C}$ from *m*-hydroxybenzaldehyde (1:0055) in AcOH with excess Cl_2 see (1) (2).]

[For condens. of $\bar{C}$ with 2,4-dichlorophenol (3:0560) see (4), with 2,4-dihydroxybenzoic acid (1:0843) and use of prod. as dye intermediate see (5).]

$\bar{C}$ in 50% aq. KOH warmed for 4 hrs. at 60–70° gives (89.9% yield (3)) 2,4,6-trichlorophenol (3:1673).

$Na\bar{A}$, pure yel. ndls., spar. sol. aq (2).

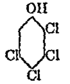
$\bar{C}$ in Na_2CO_3 soln. with Me_2SO_4 yields 2,4,6-trichloro-3-methoxybenzaldehyde, ndls. from alc., m.p 76° (2); on very slow oxidn with alk. $KMnO_4$ this prod. yields 2,4,6-trichloro-3-methoxybenzoic acid, m.p. 109° (2)

Ⓓ **2,4,6-Trichloro-3-hydroxybenzaldoxime:** ndls. from dil. alc., m.p. 174° (2), 170° (6). [This with boilg. Ac_2O yields 2,4,6-trichloro-3-acetoxybenzonitrile, lfts. from dil. AcOH, m.p. 82–83° (6).]

Ⓓ **2,4,6-Trichloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** yel.-or. ndls., m.p. 272–273° dec (2) [From $\bar{C}$ in alc with *p*-nitrophenylhydrazine + 1 drop aq. (2).]

3:3520 (1) Bissell, Kranz (to Nat. Aniline & Chem. Co.), U S 1,776,803, Sept. 30, 1930; *Cent.* **1931**, I 159; *C.A* **24**, 5769 (1930). (2) Hodgson, Beard, *J. Chem. Soc.* **1926**, 148–149, 153. (3) Lock, *Monatsh.* **55**, 312 (1930). (4) I.G., Swiss 137,923–137,929, incl., 138,180–138,183, incl., April 16, 1930, *Cent.* **1930**, II 1453. (5) Weiler (to F. Bayer & Co), U.S. 1,532,790, April 7, 1925; *Cent.* **1925**, II 352. (6) Krause, *Ber.* **32**, 123 (1899).

3:3523 2,3,4,5-TETRACHLOROPHENOL



$C_6H_2OCl_4$ Beil. S.N. 522

M.P. 116–117° (1)
116° (2) (3)

[For prepn. of $\bar{C}$ from 2,3,4,5-tetrachloroaniline [Beil. XII-630, XII_1-(313)] via diazotization and reaction with aq (65% yield) see (1); from 2-amino-3,4,5,6-tetrachlorophenol [Beil. XIII-386] (3) via diazotization and elimination of diazo group with alc. see (3); for formn. of $\bar{C}$ from pentachlorobenzene (3:2290) with $N/2$ MeOH/NaOMe at 180° in s t. for 7½ hrs. as by-prod. of the isomeric 2,3,5,6-tetrachlorophenol (3:3460) see (4).]

$\bar{C}$ in aq. behaves as an acid, K at 25° = 1.1×10^{-7}, and can be titrated with $N/10$ aq. NaOH (1), Neut Eq = 232.

—— **2,3,4,5-Tetrachlorophenol methyl ether (2,3,4,5-tetrachloroanisole):** m.p. 83° (3). [Reported only by indirect means (4).]

—— **2,3,4,5-Tetrachlorophenol ethyl ether (2,3,4,5-tetrachlorophenetole):** unreported.

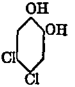
—— **2,3,4,5-Tetrachlorophenyl acteate:** unreported.

Ⓓ **2,3,4,5-Tetrachlorophenyl benzoate:** m.p. 110° (4) (5). [Note that this prod. depresses m.p. of corresp. benzoate from the isomeric 2,3,4,6-tetrachlorophenol (3:1687) (5).]

—— **2,3,4,5-Tetrachlorophenyl *N*-phenylcarbamate:** unreported.

3:3523 (1) Tiessens, *Rec. trav. chim.* **50**, 115–116, 119 (1931). (2) Tiessens, *Rec. trav. chim.* **48**, 1068 (1929). (3) Bures, Havlinova, *Časopis Československ. Lékárnictva*, **9**, 101–107, 129–134, 153–157 (1929); *Cent.* **1929**, II 1403; *C.A.* **24**, 2998 (1930). (4) Holleman, van der Hoeven, *Rec. trav. chim.* **39**, 748 (1920). (5) Holleman, *Rec. trav. chim.* **40**, 318–319 (1921).

3:3525 4,5-DICHLOROCATECHOL (4,5-Dichloropyrocatechol)



$C_6H_4O_2Cl_2$ Beil. VI - 783
VI₁-(389)
VI₂—

M.P. 116–117° (1)
105–106° (2) (3)
(See text)

Colorless pr. from $CHCl_3 + CS_2$ (1); ndls. from C_6H_6 + pet. ether (2). — $\bar{C}$ is eas. sol. in cold aq. from which it crystallizes as a hemihydrate (1) (it is possible that the m.p. of 105–106° observed by some workers may have been due to formn. of this prod.). — $\bar{C}$ cryst. from AcOH with 1 mole of solvent, viz., $\bar{C}$.AcOH (1).

[For prepn. of $\bar{C}$ from pyrocatechol (1:1520) with SO_2Cl_2 (2 moles) or from 4-chloropyrocatechol (3:2470) with SO_2Cl_2 (1 mole) see (2).]

[$\bar{C}$ with silver oxide in dry ether gives (1) 4,5-dichlorobenzoquinone-1,2 [Beil. VII₁-(338)], m.p. 94°; note, however, that $\bar{C}$ with this prod. forms a corresp. quinhydrone, dec. abt. 85°.]

[$\bar{C}$ with Cl_2 in AcOH gives (1) 3,4,5-trichloropyrocatechol (3:3448) cryst. from aq. as monohydrate, m.p. abt. 106–109° (1), 104–105° (4), 115° (5).]

[$\bar{C}$ with PCl_5 gives (2) 1,2,4,5-tetrachlorobenzene (3:4115).]

$\bar{C}$ with N/10 aq. KOH titrates (1) as a monobasic acid, i.e., Neut. Eq. = 89.5. — $\bar{C}$ with aq. $FeCl_3$ gives blue-green coloration becoming red on addn. of aq. Na_2CO_3 (1).

$\bar{C}$ does *not* (6) condense with xanthydrol (1:5205) in AcOH (dif. from 4-chloropyrocatechol (3:2470)).

—— 4,5-Dichloropyrocatechol diacetate: unreported.

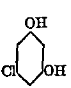
Ⓓ 4,5-Dichloropyrocatechol dibenzoate [Beil. IX₁-(72)]: m.p. 140.0–140.5° (1).

—— 4,5-Dichloropyrocatechol 1-methyl ether (4,5-dichloroguaiacol) [Beil. VII-783]: ndls. from pet. ether, m.p. 71–72° (7). [Prepd. indirectly (7).]

—— 4,5-Dichloropyrocatechol dimethyl ether (4,5-dichloroveratrole) [Beil. VII-783]: ndls. from alc., m.p. 85.5–86 5° (7). [From the preceding monomethyl ether with MeI + aq. KOH (7).]

3:3525 (1) Willstätter, Müller, *Ber.* **44**, 2184–2186 (1911). (2) Peratoner, *Gazz. chim. ital.* **28**, I 222–224 (1898). (3) Frejka, Sefranek, Zika, *Collection Czechslov. Chem. Commun.* **9**, 243–244 (1937). (4) Cousin, *Bull. soc. chim.* (3) **13**, 719 (1895); *Ann. chim.* (7) **13**, 483 (1898). (5) Jackson, Boswell, *Am. Chem. J.* **35**, 526–527 (1906). (6) Fabre, *Ann. chim.* (9) **18**, 115 (1922). (7) Peratoner, Ortoleva, *Gazz. chim. ital.* **28**, I, 229–232 (1898).

3:3530 5-CHLORORESORCINOL



$C_6H_5O_2Cl$ Beil. VI —
VI₁—
VI₂-(819)

M.P. 117° (1)

$\bar{C}$ cryst. from C_6H_6 in colorless ndls. of monohydrate, m p. 67° (1), which on sublimation in vac. yield anhydrous $\bar{C}$ (1).

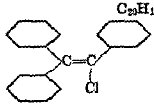
$\bar{C}$ is readily sol. in all usual solvents except lt. pet.; it rapidly absorbs aq. regenerating above monohydrate, m.p. 67° (1).

$\bar{C}$ with $FeCl_3$ gives bluish-purple color; $\bar{C}$ reduces boilg. Fehling soln.

$\bar{C}$ on bromination (no details (1)) yields 5-chloro-2,4-tribromoresorcinol, colorless ndls. from AcOH or dil. alc., m.p. 143° (1).

3:3530 (1) Hodgson, Wignall, *J. Chem. Soc.* **1926**, 2827.

3:3560 1-CHLORO-1,2,2-TRIPHENYL-ETHYLENE ("Chlorotriphenylethylene") $C_{20}H_{15}Cl$ Beil. V - 722, V_1-(355), V_2—



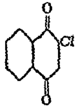
M.P. 117° (1) (2) (3) (4) (5)
116-117° (6)

Colorless cryst. from alc or pet. ether. — Insol aq.; sol. alc. or lt. pet.; freely sol. ether, acetone, benzene, or $CHCl_3$. — [For use of $\bar{C}$ in stimulation of action of estrogenic hormones see (7), for aq. susp. of $\bar{C}$ for medicinal use see (9).]

[For prepn of $\bar{C}$ from 1,1,2-triphenylethanol-1 (benzyl-diphenyl-carbinol) [Beil. VI-721, VI_1-(354)] in AcOH by treatment with Cl_2 at 30–40°, then htg. to b.p. to remove AcOH and effect loss of HCl (87% yield), see (1); from 1,2-dichloro-1,1,2-triphenylethane (1) by htg. just above m p. (115°) (100% yield (1)) or by refluxing 5 hrs. in pyridine (65% yield (1)) see (1); from triphenylethylene [Beil V-722, V_1-(355)] in AcOH with Cl_2 (1), in C_6H_6 with PCl_5 (4), or in CCl_4 with SO_2Cl_2 in pres. of dibenzoyl peroxide (2) see indic. refs.; from ω,ω-diphenylacetophenone (1,1,2-triphenylethanone) (triphenylvinyl alcohol) [Beil. VII-522, VII_1-(291)] (5) (3) or from triphenylacetaldehyde [Beil. VII_1-(292)] (6) with PCl_5 see indic. refs.]

3:3560 (1) van de Kamp, Sletzinger, *J. Am. Chem. Soc.* **63**, 1879–1881 (1941). (2) Tadros, *Nature* **148**, 53 (1941). (3) Schönberg, Robson, Tadros, Fahim, *J. Chem. Soc.* **1940**, 1328. (4) Bergmann, Bondi, *Ber.* **64**, 1467–1468 (1931). (5) Gardeur, *Bull. acad. roy. Belg.* **34**, 67–100 (1897), *Cent.* **1897**, II 662. (6) Danilov, *J. Russ. Phys.-Chem. Soc.* **51**, 125 (1919); *Cent.* **1923**, III 761. (7) Robson, Schönberg, Fahim, *Nature* **142**, 292 (1938). (8) MacPherson, Robertson, *Lancet* (2) **237**, 1362 (1939). (9) Collie & Imperial Chem. Ind., Ltd., Brit. 543,897, March 18, 1932, *C.A.* **36**, 6313 (1942).

3:3580 2-CHLORONAPHTHO-QUINONE-1,4 (2-Chloro-α-naphthoquinone) $C_{10}H_5O_2Cl$ *Beil. VII - 729*, VII_1—



M.P. 118°	(1)
117°	(2) (3) (4)
116-117°	(5)
116°	(9)
115°	(8)
112° u.c.	(6)
111°	(7)

Yel. ndls with pungent quinone odor from dil. alc. or dil. AcOH. — Volatile with steam. — Eas. sol. alc., C_6H_6; spar. sol. ether.

[For prepn. of $\bar{C}$ from naphthoquinone-1,4 (α-naphthoquinone) (1:9040) by conversion with Cl_2 in AcOH to 2,3-dichloro-1,4-diketo-1,2,3,4-tetrahydronaphthalene ("α-naphtho-

quinone dichloride") [Beil. VII-702] and subsequent elimination of 1 HCl with NaOAc/AcOH see (4) cf. (7); from α-naphthol (1:1500) by conversion with Cl_2 in AcOH to 2,2,4-trichloro-1-keto-1,2-dihydronaphthalene [Beil. VII-387] and subsequent hydrolysis (with rearr.?) in boilg. dil. alc. or dil. AcOH see (5).]

[For prepn. of $\bar{C}$ from 1,3-dichloronaphthalene (3:1310) by oxidn. with CrO_3/AcOH see (8); from 2,4-dichloronaphthol-1 (3:3250) by oxidn. with CrO_3/AcOH or HNO_3/AcOH see (5) (9); from 2-chloro-1,2-diaminonaphthalene (2-chloronaphthylenediamine-1,2) by oxidn. with 2% alk. $KMnO_4$ see (2); from 2-chloronaphthol-1-sulfonic acid-4 by oxidn. with MnO_2 in boilg. 50% H_2SO_4 see (1); from 2,4-dinitronaphthol [Beil. VI-617, VI_1-(308)] by oxidn. with NaOCl in HCl soln. (3) or HCl + $KClO_3$ (10) see indic. refs.; from sodium salt of 4-(p-sulfobenzeneazo)naphthol-1 ("Orange I") [Beil. XVI-275, XVI_1-(296)] by oxidn. with NaOCl in HCl soln. see (3).]

[$\bar{C}$ on reduction might be expected to give 2-chloro-1,4-dihydroxynaphthalene [Beil. VI-975], m.p. 116–117°; note, however, that this reaction has not actually been reported and that this prod. is also obtained by SO_2 reduction of 3-chloronaphthoquinone-1,2 (3:4704). — For study of oxidn.-reductn. potential of $\bar{C}$ see (7).]

[$\bar{C}$ with Cl_2 in AcOH gives (4) (5) 2,3-dichloronaphthoquinone-1,4 (3:4857).]

[$\bar{C}$ in boilg. alc. with aq. NaN_3 splits out NaCl giving (90% yield (11)) 2-azidonaphthoquinone-1,4, long yel. pr. from alc., m.p. 118° dec.]

$\bar{C}$ with aniline on htg. (5) (6) in alc. soln. (8) (9) gives 3-chloro-2-anilino-naphthoquinone-1,4 [Beil. XIV-168, XIV_1-(434)], red ndls., m.p. 207–208° (10), 207° (8), 202–203° (9) (6).

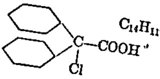
$\bar{C}$ like many other quinones is able to form Diels-Alder type adducts with many conjugated dienes [e.g., $\bar{C}$ with 2,3-dimethylbutadiene-1,3 (1:8050) gives an adduct which with aq. 5% NaOH and a little $Na_2S_2O_4$ at 70° reduces (with loss of halogen) to 2,3-dimethyl-1,4-dihydroanthrahydroquinone which in turn upon oxidn. with air at 0° gives (12) 2,3-dimethylanthraquinone [Beil. VII-815, VII_1-(425)], yel. ndls. from alc. or AcOH, m.p. 210° (13), 209° (14), 208–209° (15), 208° (16), 205–206° (17); note also that this 2,3-dimethylanthraquinone is also obtd. (18) from the initial adduct with pyridine in absence of air, or (18) from $\bar{C}$ + 2,3-dimethylbutadiene-1,3 (1:8050) at 100–105° under press. — For behavior of $\bar{C}$ with 2-methylbutadiene-1,3 (isoprene) (1:8020) and with butadiene-1,3 see (18).]

—— 2-Chloronaphthoquinone-1,4-oxime-4 (2-chloro-4-nitrosonaphthol-1) [Beil. VII-729]: ndls. from alc., m.p. 200° dec. (8). [From $\bar{C}$ with $NH_2OH.HCl$ in alc. on warming (8).]

—— 2-Chloronaphthoquinone-1,4-(p-nitrophenylhydrazone-4) = 4-(p-nitrobenzeneazo)-2-chloronaphthol-1: m.p. 274° dec. (1). [From $\bar{C}$ with p-nitrophenylhydrazine (1); also from 2-chloronaphthol-1 (3:1490) in alk. soln. on coupling with diazotized p-nitroaniline (1).]

3:3580 (2) Hodgson, Elliott,
J. Chem ..., 201, 338 (1927). (4)
Zincke, ... 1036–1039 (1888). (6)
Russig, *J. prakt. Chem.* (2) 62, 41–42 (1900).
1875 (1924). (8) Cleve, *Ber.* 23, 955 (1890).
mann, *Ber.* 15, 485, Note 1 (1882).

3:3585 α-CHLORO-DIPHENYL-ACETIC ACID
(Diphenylchloroacetic acid)



$C_{14}H_{11}O_2Cl$ Beil. IX - 674
IX_1-(282)

M.P. 120° dec. (1)
118–119° dec. (2) (3)

[*See also α-chlorodiphenylacetyl chloride* (3:0885).]

Tbls. from C_6H_6/lgr.; very eas sol. lgr.

[For prepn. of $\bar{C}$ from benzilic acid (α-hydroxydiphenylacetic acid) (1:0770) with $POCl_3$ on warming (not boilg) until red color begins to appear (65% yield (3)) (4); with PCl_5 (62 5% yield (1)) or PCl_3 (68% yield (1)) both at room temp ; with $SOCl_2$ directly at room temp. (92% yield (1)) or with $SOCl_2$ (3 moles) in CCl_4 at ord. temp (5) (2) see indic. refs ; note, however, that benzilic acid (1:0770) with PCl_5 (2 moles) at 120–130° (6) or 100° (7) or *excess* PCl_5 (5 moles) in C_6H_6 at room temp. (1) gives instead α-chlorodiphenylacetyl chloride (3:0885), m p. 50°; note also that benzilic acid (1:0770) with large excess (6 moles) $SOCl_2$ refluxed for several days gives (5) α-chlorodiphenylacetic acid anhydride [Beil. IX_1-(228)], m p 129° (5)]

[For prepn. of $\bar{C}$ from *O*-carbomethoxybenzilic acid (2) with $SOCl_2$ see (2); for prepn of $\bar{C}$ from α-chlorodiphenylacetyl chloride (3:0885) by hydrolysis (even in moist air) see (8).]

$\bar{C}$ on reduction with $TiCl_3$ in boilg. AcOH gives (8) diphenylacetic acid (1:0765), m.p. 148°.

$\bar{C}$ (or its sodium salt) htd. under reduced press. at 125° for 10 hrs. gives (80–90% yield (9)) benzilide [Beil. XIX-187, XIX_1-(700)], ndls. from alc., m.p 196° (10), 194° (11) (5), 193° (12), 192–193 5° (9) [the structure of this prod is disputed, but it is either 2,2,5,5-tetraphenyl-3,6-diketodioxane-1,4 or tetraphenyldiglycolic acid anhydride].

$\bar{C}$ with aq. KSH (or NaSH) does *not* (21) give the expected α-mercaptodiphenylacetic acid (diphenylthioglycolic acid) (thiobenzilic acid) [Beil X_1-(154)], but rather (apparently because of alkalinity of the soln) benzilic acid (1·0770).

[$\bar{C}$ with NaOMe (?) gives (13) α-methoxydiphenylacetic acid (benzilic acid *O*-methyl ether) [Beil. X_1-(152)], m.p. 100° (13); note that various compounds prepd by a wide variety of methods but all supposed to have this structure have been reported with m p.'s as follows: 99–100° (14), 102° (15), 106° (16), 107° (17), 111–112° (18), 120–121° (9); note also that the corresp. methyl ester, viz., methyl α-methoxydiphenylacetate, oil, b p 199–200° at 27 mm., has been prepd. (19) from α-bromodiphenylacetate with MeOH.]

[$\bar{C}$ with EtOH/NaOEt gives (8) cf. (13) α-ethoxydiphenylacetyl bromide with MeOH.] tbls. from ether, m.p. 114–115° (20) (8), 114° (13), 113–114° (14); the corresp. ethyl ester, viz., ethyl α-ethoxydiphenylacetate, appears to be unreported]

$\bar{C}$ with Na phenolate might be expected to give α-phenoxydiphenylacetic acid, but neither this reaction nor the expected prod. is reported. — However, $\bar{C}$ with thiophenol in C_6H_6 refluxed 2 hrs evolves HCl and gives (22) α-thiophenoxy-diphenylacetic acid, cryst. from 50% AcOH, m p. 126–128° (22)

[$\bar{C}$ with C_6H_6 + $AlCl_3$ gives normal Friedel-Crafts type reaction giving (25% yield (3)) triphenylacetic acid [Beil. IX-712, IX_1-(309)], m p. 265°.]

$\bar{C}$ with various amines or amino compds splits out HCl giving the corresp. α-aminodiphenylacetic acid derivatives [e.g , $\bar{C}$ with NH_3 gives (13) α-aminodiphenylacetic acid (diphenylglycine), m p. 245° (13); $\bar{C}$ with piperidine gives (13) α-piperidinodiphenylacetic acid, m p. 180° (13); for other cases see (13)].

$\bar{C}$ with benzhydrazide in C_6H_6 splits out HCl and yields (8) α-benzhydrazido-diphenylacetic acid, m.p. 167–168° (8).

$\bar{C}$ with excess $SOCl_2$ on warming does *not* give the expected α-chlorodiphenylacetyl chloride (3:0885), m.p. 50°, but rather (5) α-chlorodiphenylacetic acid anhydride, m.p. 120° (5).

$\bar{C}$ in pyridine on htg. at 100° (23) evolves CO_2 presumably yielding benzohydryl chloride (α-chlorodiphenylmethane) (3:0060) as its quaternary salt with pyridine.

—— Methyl α-chlorodiphenylacetate: oil, b.p. 196° at 16 mm. (4). [From $\bar{C}$ in dioxane soln. with diazomethane (100% yield) (4); note also that this ester with Cu bronze refluxed in C_6H_6 for 5 hrs. then evaporated in air gives (4) the *peroxide*, m.p. 151–152°, of dimethyl tetraphenylsuccinate.]

—— Ethyl α-chlorodiphenylacetate: cryst. from alc., m.p. 43–44° (24) (6), b.p. 185° at 14 mm. (24). [From $\bar{C}$ with EtOH + dry HCl (10) best in pres. of C_6H_6 as directed (90% yield (25)), or from α-chlorodiphenylacetyl chloride (3:0885) with EtOH (6), or from ethyl benzilate (1:2086) with PCl_5 (6).]

—— α-Chlorodiphenylacetamide: m.p. 115° (6), 111–113° (26). [From α-chlorodiphenylacetyl chloride (3:0885) in ether with NH_3 gas (6) (13).]

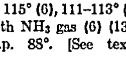
—— α-Chlorodiphenylacetanilide: m.p. 88°. [See text of α-chlorodiphenylacetyl chloride (3:0885).]

3:3585 (1) Setlur, Nadkarny, *Proc. Indian Acad. Sci.* **12-A**, 268 (1940); *C.A.* **35**, 1398 (1941).

... (12) Staudinger, *Ber.* **44**, 545–547 (1911). (13) ... 12-A, Pt. 3, 68–70 (1943); *C.A.* **38**, 3250, 1739 ... *Ann.* **464**, 38 (1928). ... 56, ... ijise, ... 114); ...

... 465–466 (1920). (22) Bistrzycki, Risi, *Helv.* ... *Veneto sci.*, Ser. II, **94**, 167–182 (1935): *Cent.* **1937**, II 3605; not in *C.A.* (24) Klinger, *Ann.* **389**, 262–263 (1912). (25) Adickes, *J. prakt. Chem.* (2) **150**, 91 (1938). (26) Steinkopf, *Ber.* **41**, 3593 (1908).

3:3590 PENTACHLOROBENZAL (DI)CHLORIDE



C_7HCl_7 Beil. V - 304, V_1-(153), V_2—

M.P. 119.5° (1) **B.P.** 334° (2)
109° (2) 109° cor. at 13 mm. (3)

Colorless lfts. from alc.; eas. sol. hot, spar. sol. cold, alc.

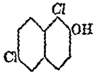
[For prepn. of $\bar{C}$ ... (3:4037) with Cl_2 at 210–230° as directed (70–80% y... ...l (di)chloride (3:6327) with Cl_2 in pres. of I_2 + ... " [Beil. VII-576, VII_1-(323)] with PCl_5 (2 moles) at 230° for 12–16 hrs. (together with hexachlorobenzene (3:4939)) see (1).]

$\bar{C}$ is unaffected by aq. even in s.t. at 300°; however, $\bar{C}$ on hydrolysis with conc. H_2SO_4

at 60–100° or with fumg. H_2SO_4 at 40–50° gives (90% yield (3)) (4) pentachlorobenzaldehyde (3:4892), m.p. 202.5° (3).

3:3590 (1) Zincke, von der Linde, *Ber.* **26**, 318 (1893). (2) Beilstein, Kuhlberg, *Ann.* **150**, 306–308 (1869). (3) Lock, *Ber.* **66**, 1533 (1933). (4) Bayer and Co., Ger. 243, 416, Feb. 10, 1912, *Cent* **1912**, I 618, [*C.A.* **6**, 2292 (1912)]; U.S. 998,140, July 18, 1911; [*C.A.* **5**, 2904–2905 (1911)].

3:3600 1,6-DICHLORONAPHTHOL-2



$C_{10}H_6OCl_2$ Beil. VI — VI_1— VI_2-(604)

M.P. 119.5° (1)

Ndls from hot lgr.

[For prepn from 1-chloronaphthol-2 (3:1700) by actn. of Cl_2 in sunlight see (1).]

$\bar{C}$ on reduction with $FeSO_4$ + NaOH yields (2) 6-chloronaphthol-2 (3:3500), m.p. 115° (2).

3:3600 (1) Ruggli, Knapp, Merz, Zimmermann, *Helv. Chim. Acta* **12**, 1050–1051 (1929). (2) Herzberg, Spengler, Schmidt (to I G), Ger. 431,165, June 30, 1926, *Cent.* **1926**, II 1196.

3:3634 DICHLOROMALEIC ACID

Cl—C—COOH
‖
Cl—C—COOH

$C_4H_2O_4Cl_2$ Beil. II - 753 II_1— II_2—

M.P. 119–120° (1)
118.5–119° (2)
118–119° (3)
116° (4)

[*See also dichloromaleic anhydride* (3:3635) *and dichloromaleyl (di)chloride* (3:6197).]

Ndls. from lgr./ether. — Eas. sol. aq.; sol. alc., AcOH; insol C_6H_6, $CHCl_3$, CS_2. — Note that $\bar{C}$ on htg. very readily loses H_2O and is converted to dichloromaleic anhydride (3:3635); the m.p.'s observed for $\bar{C}$ are probably actually those of its anhydride.

Note also that, although the structure corresp. to $\bar{C}$ should be capable of existing also in the geometrically isomeric *trans* configuration, no such dichlorofumaric acid or its derivatives has ever been reported.

[For prepn. of $\bar{C}$ from furfural (1:0185) in conc. HCl soln. with Cl_2 (30% yield) see (5); from dichloromaleinaldehyde-acid ("mucochloric acid") [Beil. III-727] by oxidn. with fumg. HNO_3 on stdg. at ord. temp. for several days (100% yield (4)) (2) see indic. refs.; from α,β-dichloro-β-(trichloroacetyl)acrylic acid ("perchloro-β-acetylacrylic acid") [Beil. III-733] by hydrolytic cleavage with aq. NaOH (chloroform is also formed) see (3); from hexachlorocyclohexen-1-dione-3,6 [Beil. VII-574] by hydrolytic cleavage with 10% aq. NaOH (trichloroethylene (3:5170) is also formed) see (1); from hexachlorocyclohexen-1-dione-3,5 ("hexachlororesorcinol") (3:3470) (6) or from 2,2,3,4,6,6,6-heptachlorohexen-3-one-5-acid-1 [Beil. III-735, III_1-(255)] (6) with large excess dil. aq. $Ca(OCl)_2$ see indic refs.]

[For formn. of $\bar{C}$ from 3,4-dichlorofuroic acid [Beil. XVIII-282] by oxidn. with boilg. dil. HNO_3 (7) or from 3,4,5-trichlorofuroic acid [Beil. XVIII-283] by oxidn. with hot dil. HNO_3 or cold Br_2/aq. (7) see indic. refs.; from pyrrole with aq. NaOCl (other prods. are also formed) see (8).]

$\bar{C}$ behaves normally as a dibasic acid: e.g., $\bar{C}$ on titration with standard dil. aq. alk. gives Neut. Eq. 92.5 (2).

[Salts: for $Li_2\bar{A}$, $Na_2\bar{A}.H_2O$, $NaH\bar{A}.H_2O$, $K_2\bar{A}.2H_2O$, $K_2\bar{A}.H_2O$, $Cu\bar{A}.H_2O$, $Pb\bar{A}.H_2O$, $Ni\bar{A}.2H_2O$ see (4). — $Ba\bar{A}.2\frac{1}{2}H_2O$ (3). — $Ag_2\bar{A}$, white ndls. which explode on htg. (3) (8) (9).]

—— **Dimethyl dichloromaleate:** oil, b.p. 225° (9). [From dichloromaleic anhydride (3:3635) in MeOH with HCl gas on boilg. (9). — This prod. with aniline at 100° yields (4) dimethyl α,β-dianilinomaleate, cryst. from alc., m.p. 172° (4).]

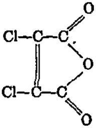
—— **Diethyl dichloromaleate:** unreported.

—— **Dichloromaleinimide** [Beil. XXI-401]: ndls. from aq., m.p. 179° (10). [From dichloromaleic anhydride (3:3635) with urea on htg. at 110–115° (10).]

—— ***N*-Phenyldichloromaleinimide** *(dichloromaleanil)* [Beil. XXI-402]: *colorless lfts.* from MeOH, m.p. 203°. [Reported only by indirect means.]

—— **Dichloromaleic dianilide:** see under text of dichloromaleyl (di)chloride (3:6197).

3:3634 (1) Zincke, Fuchs, *Ann.* **267**, 19–22 (1892). (2) Stelling, *Z. physik. Chem.* **B-24**, 424 (1934). (3) Zincke, von Lohr, *Ber.* **25**, 2230 (1892). (4) Salmony, Simonis, *Ber.* **38**, 2588–2590, 2594–2595, 2598–2599 (1905). (5) Leder, Russ. 48,297, Aug. 31, 1936; *Cent.* **1937**, II 288. (6) Zincke, Fuchs, *Ber.* **26**, 509–510 (1893). (7) Hill, Jackson, *Am. Chem. J.* **12**, 43–44, 124–125 (1890). (8) Ciamician, Silber, *Ber.* **17**, 1743–1744 (1884). (9) Kauder, *J. prakt. Chem.* (2) **31**, 5–6 (1885). (10) Dunlap, *Am. Chem. J.* **18**, 333–334 (1896).

3:3635 DICHLOROMALEIC ANHYDRIDE  $C_4O_3Cl_2$ Beil. XVII-434 XVII₁—

M.P. **119–120°** (1) (2)
119.5° (3)
119° (4) (8)
117–118° (5)

[*See also dichloromaleic acid* (3:3634).]

Colorless lfts. very eas. sol. alc., ether, C_6H_6, or CS_2; sublimable.

[For prepn. of $\bar{C}$ from dichloromaleic acid (3:3634) by htg. see (1) (2) (10); for prepn. of $\bar{C}$ from maleic anhydride (1:0625) with Cl_2 at 130° in pres. of Fe (80% yield (7)) or from chlorofumaryl dichloride with Cl_2 in pres. of Fe (8) see indic. refs.; for prepn. of $\bar{C}$ from furoic acid (1:0475) by conv. with MnO_2 + HCl to mucochloric acid, OCH.CCl=CCl.COOH [Beil. III-727] (9), and subsequent treatment with fumg. HNO_3 (4) (9) or from 3,4-dichlorofuran (9) by oxidn. with fumg. HNO_3 (9) see indic. refs.; for formn. of $\bar{C}$ (together with other products) from diethyl tartrate (1:4256) with PCl_5 for 7–8 hrs. at 100° see (6); from either dichloromaleo(di)nitrile (m.p. 58–59°, D_4^{62} = 1.32501, n_D^{62} = 1.48824 (12)) or from dichlorofumaro(di)nitrile (m.p. 60.0–60.5°, D_4^{62} = 1.32543, n_D^{62} = 1.48845 (12)) by hydrol. see (12).]

$\bar{C}$ is itself spar. sol. aq. but slowly dissolves (1) (6) yielding a soln. of dichloromaleic acid (3:3634).

$\bar{C}$ with PCl_5 yields (8) dichloromaleyl dichloride (3:6197).

$\bar{C}$ with 1 mole anthracene (1:7285) htd. for 10 min. at 170° gives 100% yield (4) of anthracene-9,10-*endo*-dichloromaleic anhydride, ndls. from acetonitrile, m.p. 235° (4).

$\bar{C}$ with 1 mole urea htd. to 90–95° for 20 min. yields (11) dichloromaleic acid monoureide [Beil. III-68], m.p 158° dec. (11); this prod. on fusion or the original system htd. at 110–115° yields (11) dichloromaleinimide [Beil. XXI-401], m.p. 179° (11).

$\bar{C}$ on htg. with aniline (9) yields α-chloro-α-anilinomalein-α′-isoanil [Beil. XVII-555], greenish yel. cryst. from alc., m.p. 188.7–190 2° cor. (9), 187° (10).

3:3635 (1) Ciamician, Silber, *Ber.* **16**, 2396 (1883) (2) Zincke, Fuchs, *Ann.* **267**, 20–22 (1892). (3) Kauder, *J. prakt Chem* (2) **31**, 4 (1885) (4) Diels, Thiele, *Ber.* **71**, 1173–1178 (1938). (5) Leder, *J prakt Chem* (2) **130**, 271 (1931) (6) Patterson, Todd, *J. Chem. Soc* **1929**, 1768–1771. (7) Leder, Russ 43,419, June 30, 1935, *Cent.* **1936**, I 1310, *C A.* **31**, 7447 (1937). (8) Vandevelde, *Bull. acad. roy Belg* (3) **37**, 680–700 (1900); *Cent* **1900**, I 404. (9) Shepard, Winslow, Johnson, *J. Am Chem Soc.* **52**, 2088–2089 (1930). (10) Salmony, Simonis, *Ber.* **38**, 2588 (1905).

(11) Dunlap, *Am Chem J* **18**, 333–334 (1896) (12) Mommaerts, *Bull classe sci., Acad. roy. Belg.* (5) **27**, 579–597 (1944), *Cent* **1943**, I 615–616, *C.A.* **38**, 3621 (1944).

3:3665 2,3-DICHLORONAPHTHALENE  $C_{10}H_6Cl_2$ Beil. V - 544
V_1—
V_2-(446)

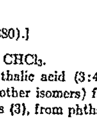
M.P. 120° (1)
119.5–120.5° (2)
119.5° (4)

Spar. sol cold, eas sol hot alc or ether.

[For prepn of $\bar{C}$ from naphthalenetetrachloride-1,2,3,4 (3:4750) by htg. with Ag_2O in s.t. at 200° (1) or (in small yield together with other prods.) by boilg. with alc. KOH (3) (4) see indic. refs; from 1,2,3-trichloronaphthalene (3:2125) with Na/Hg in alc. see (4).]

[$\bar{C}$ on monosulfonation in CS_2 with $ClSO_3H$ yields (4) mainly 2,3-dichloronaphthalene-sulfonic acid-8 [Beil. XI-164] (corresp. sulfonyl chloride, m.p. 142°, corresp. sulfonamide m.p. 268°) accompanied by 2,3-dichloronaphthalenesulfonic acid-6 (?) [Beil. XI-183] (corresp. sulfonyl chloride, m p. 178°).]

3:3665 (1) Leeds, Everhart, *J. Am. Chem Soc.* **2**, 210–212 (1880). (2) Hampson, Weissberger, *J. Chem. Soc.* **1936**, 394. (3) Widman, *Ber.* **15**, 2162 (1882). (4) Armstrong, Wynne, *Chem. News* **61**, 273–275, 284 (1890).

3:3695 3,4-DICHLOROPHTHALIC ANHYDRIDE  $C_8H_2O_3Cl_2$ Beil. XVII - 483
$XVII_1$-(253)

M.P. 120–121° cor. (1)
120–121° (2)

[*See also 3,4-dichlorophthalic acid* (3:4880).]

Tbls. from CCl_4; sol. in C_6H_6, toluene, $CHCl_3$.

[For prepn. of $\bar{C}$ from 3,4-dichlorophthalic acid (3:4880) by protracted htg. at 220° see (2); for formn. of $\bar{C}$ (together with other isomers) from phthalic anhydride (1:0725) with Cl_2 at 240° in pres of Fe or Fe salts (3), from phthalic anhydride or 3-chlorophthalic

anhydride (3:3900) with Cl_2 in fumg. H_2SO_4 in pres. of I_2 (4) (1), see indic. refs.] [For sepn. of $\bar{C}$ from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids see (4) (1) (18); by means of differential hydrolysis with H_2SO_4 (prods. with no α-chlorine such as 4,5-dichlorophthalic anhydride require H_2SO_4 of 98–100% concn.; those with one α-chlorine such as $\bar{C}$ hydrolyze with 56–95% H_2SO_4; those with two α-chlorines such as *3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at H_2SO_4 concns. of* less than 50%) see (5).]

$\bar{C}$ dislvd. in abs. alc. yields *one* of the two known acid esters, viz., 3,4-dichloro-2-carbethoxybenzoic acid, pr. from dil. alc., m.p. 164° (6); see also under 3,4-dichlorophthalic acid (3:4880).

[$\bar{C}$ with PCl_5 htd. in s.t. at 200° for 6 hrs. gives exclusively (6) *pseudo*-3,4-dichlorophthaloyl dichloride (3,3,6,7-tetrachlorophthalide), ndls. from C_6H_6, m.p. 133° (6) (this prod. shaken *with abs. alc. susp. of $CaCO_3$ for 10 hrs. yields (6)* 6,7-dichloro-3,3-diethoxyphthalide, pr. from pet. ether., m.p. 79° (6), which depresses m.p. of normal diethyl 3,4-dichlorophthalate, m.p. 80° (6) to 60°).]

$\bar{C}$ with 1 mole $NH_2OH.HCl + Na_2CO_3$ in aq. as directed (2) yields 3,4-dichlorophthalylhydroxylamine (*N*-hydroxy-3,4-dichlorophthalimide) [Beil. XXI-504], ndls. from MeOH, m.p. 218–219° (2), 216–219° (7) (this prod. with boilg. aq. Na_2CO_3 yields (2) (7) a mixt. of 3,4-dichloro-2-aminobenzoic acid (3,4-dichloroanthranilic acid) [Beil. XIV-367, XIV_1-*(549)] and 5,6-dichloro-2-aminobenzoic acid (5,6-dichloroanthranilic acid* [Beil. XIV-368]).

[$\bar{C}$ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (8) 2,3-dichlorobenzoic acid (3:4650) and/or 3,4-dichlorobenzoic acid (3:4925).]

[$\bar{C}$ with hydroquinone (1:1590) + H_3BO_3 htd. at 190° and afterward treated with hot conc. H_2SO_4 (9), or $\bar{C}$ with $AlCl_3$ + NaCl htd. at 200–220° for 45 min. (10), or $\bar{C}$ with *p*-chlorophenol (3:0475) htd. with fumg. $H_2SO_4 + H_3BO_3$ (11), gives 5,6-dichloro-1,4-dihydroxyanthraquinone *(5,6-dichloroquinizarin) [Beil. $VIII_1$-(715)], red. ndls. from* AcOH, m.p. 239° (10), 208° (9) (diacetate, m.p. 170° (10), 140° (9)).]

[For study of behavior of $\bar{C}$ with *o*-chlorotoluene + $AlCl_3$ see (12); for use of $\bar{C}$ with dibenzanthrone derivs. in prepn. of vat dyes see (13); for reactn. with *p*-cresol see (16).]

$\bar{C}$ on fusion with urea yields (14) 3,4-dichlorophthalimide, m.p. 348–351° (14) (for use in prepn. of pigments of phthalocyanine type see (14) (15)).

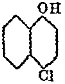
$\bar{C}$ (1 pt.) dislvd. in 5 pts. boilg. AcOH and treated with 1 pt. aniline gives on cooling *97% yield 3,4-dichlorophthalanil [Beil. XXI_1-(391)], cryst. from AcOH, m.p. 181–181.5°* cor. (1), ndls. from alc., m.p. 179–180° (17) [note, however, that on protracted htg. with excess aniline one of the two nuclear halogens also reacts, e.g., $\bar{C}$ (1 pt.) boiled with 3 pts. aniline for 10 hrs. gives 4-chloro-3-anilinophthalanil, cryst. from alc., m.p. 159.5–160° cor. (1); note also that under certain conditions both halogens can be removed, e.g., 3,4-dichlorophthalanil (above) on refluxing 6 hrs. with aniline + anhydrous Na_2CO_3 + Cu gives (10% yield (17)) 3-anilinophthalanil, or.-yel. pr., m.p. 144.5–145° (17).]

$\bar{C}$ on saponification with standard alk. (Sap. Eq. = 108.5), followed by acidification, yields 3,4-dichlorophthalic acid (3:4880) q.v.

3:
25
19
Fr
68
(tc
13
I:

I 2533; 1930, I 1303. (13) Imperial Chem. Ind., Ltd., Shaw, Thomson, Brit. 383,624, Dec. 15, 1931; *Cent.* 1933, I 1358. (14) Imperial Chem. Ind., Ltd, Thorpe, Linstead, Brit 390,149, Apr. 27, 1933: French 737,392, Dec. 10, 1932, *Cent.* 1933, II 794. (15) Thorpe, Linstead, Thomas (to Scottish Dyes, Ltd.), Brit. 389,842, Apr. 20, 1933; *Cent.* 1933, II 3769. (16) Knesebeck, Ullmann, *Ber.* 55, 306, 315 (1922). (17) Mariott, Robinson, *J. Chem. Soc.* 1939, 137. (18) Hodgson, *J. Soc. Dyers Colourists* 49, 215 (1933).

3:3720 4-CHLORONAPHTHOL-1 $C_{10}H_7OCl$ Beil. VI - 611
VI_1-(308)
VI_2-(582)



M.P. **120–121°** (1)
120–120.5° (2)
120° (3)
116–117° (4) (26)
116° (5)

Ndls. from dil. alc. or from $CHCl_3$. — Very eas. sol. org. solv. — Sublimes in ndls. — Volatile with steam but less so than 2-chloronaphthol-1 (3:1490) (use in sepn. from latter (6)).

[For prepn. of C̄ from *bis*-(4-chloronaphthyl-1) carbonate (itself obtd. from *bis*-(α-naphthyl) carbonate in AcOH with Cl_2 in pres. of $SbCl_3$ (5)) by hydrolysis with alc. KOH see (5); from 4-chloronaphthyl-1 *p*-toluenesulfonate (itself obtd. from α-naphthyl *p*-toluenesulfonate in CCl_4 with Cl_2 + cat. (7)) by hydrolysis see (7); from α-naphthol (1:1500) with SO_2Cl_2 in $CHCl_3$ as directed (yields: 20–60% (1), 42% (6), 27–33% (8)) (26) (the isomeric 2-chloronaphthol-1 (3:1490) is also formed) see indic. refs.; from 1,4-dichloronaphthalene (3:1655) by htg. with MeOH/KOH in copper-lined autoclave 20 hrs. at 190–200° see (9); from 4-chloronaphthol-1-sulfonic acid-8 (10) (3) by hydrolysis (10) or reductive cleavage with Na/Hg (3) of the $-SO_3H$ group see indic. refs.; from 4-chloro-1-hydroxynaphthoic acid-2 [Beil. X_1-(146)] by htg. in naphthalene or nitrobenzene in pres. of aniline (yield: 81–89%) see (2); from 4-chloronaphthyl-1 MgBr in ether by oxidn. with dry O_2 see (4).]

C̄ with Cl_2 in AcOH yields (4) 2,4-dichloronaphthol-1 (3:3250), m.p. 106° (4); C̄ with 1 mole Br_2 in AcOH gives alm. quant. yield (11) 2-bromo-4-chloronaphthol-1; ndls., m.p. 96° (11).

[C̄ with 0.5 mole SCl_2 in $CHCl_3$ gives (79% yield (12)) *bis*-(4-chloro-1-hydroxynaphthyl-2) sulfide, colorless ndls. from hot alc., m.p. 172° dec. (12); for reactn. of C̄ with 2-hydroxynaphthalene-1-sulfenyl bromide (13) (14), or with SCl_2 + β-naphthol (15), see indic. refs.]

[C̄ undergoes many condensations with various types of cpds., e.g., for condensation of C̄ with formaldehyde (16) (17), with 2,6-*bis*-(hydroxymethyl)-4-methylphenol (18), and use of prods. as mothproofing cpds. see indic. refs.; for condensation of C̄ with naphthalene-2,3-dicarboxylic acid anhydride [Beil. $XVII_1$-(266)] see (19); for condensation of C̄ with malic acid (1:0450) or with ethyl acetoacetate (1:1710) or with ethyl methylacetoacetate (1:1712) using H_2SO_4 or P_2O_5 yielding naphthapyrone derivs. see (8); for condens. of C̄ with 2,3-dichloronaphthoquinone-1,4 (3:4857) for use in prepn. of vat dyes see (21).]

[C̄ with maleic anhydride (1:0625) + $AlCl_3$ + NaCl htd. ½ hr. at 210–220° gives (12% yield (20)) 10-chloro-1-hydroxyanthraquinone-4,9, dark red ndls. from C_6H_6, m.p. 205–206°; similarly C̄ with citraconic anhydride (1:1135) yields (20) both 10-chloro-1-hydroxy-2-methyl- and 10-chloro-1-hydroxy-3-methylanthraquinone-4,9.]

[$\bar{C}$ with 2,4-dinitrotoluene forms a mol. cpd., m.p. 65° (22); $\bar{C}$ with 2,4-dinitroanisole forms a mol. cpd. (22); for use of these as fungicides see (22); for use of $\bar{C}$ as disinfectant see (23).]

$\bar{C}$ with PkOH in $CHCl_3$ (5) forms an unstable mol. cpd., $\bar{C}$.PkOH, or. ndls., m.p. 171° (5), 170–171° (4) (1).

$\bar{C}$ with $FeCl_3$ or $Ca(OCl)_2$ in neutral soln. gives blue ppt. (5) (4).

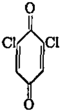
$\bar{C}$ in alc. (10 pts.) treated with conc. HCl (5 pts.) and then with $NaNO_2$ (0.4 pt.) yields (2) 4-chloronaphthoquinone-1,2-oxime-2 [Beil. VII$_1$-(385)], purified via the beautifully crystg. dif. sol. red sodium salt, from which HCl ppts. the free oxime, pale yel. ndls, m.p. 157° (2).

Ⓓ **4-Chloro-1-naphthyl acetate:** cryst. from lgr., m.p. 44° (4) (26). [From $\bar{C}$ with AcCl (2).] [For Fries rearr. of this acetate to 4-chloro-1-hydroxy-2-naphthyl methyl ketone see (24).]

—— **4-Chloro-1-naphthyl benzoate:** ndls. from alc., m.p. 100–101° (25). [Reported only by indirect means (25).]

3:3720 (1) Kast, *Ber.* **44**, 1337 (1911). (2) Reissert, *Ber.* **44**, 867–869 (1911). (3) Friedländer, Karamessinis, Schenk, *Ber.* **55**, 50 (1922). (4) Bodroux, *Bull. soc. chim.* (3) **31**, 35–36 (1904). ... –3053 (1895). (6) Lesser, Gad, *Ber.* **56**, 972–973 (1923). ... Ger. 240,038, Oct. 20, 1911; *Cent.* **1911**, II 1565. (8) ... *Soc.* **13**, 651–653 (1936). (9) Soc. d'exploitation des brevets O. Matter, French 807,536, Jan. 14, 1937; *Cent.* **1937**, I 4560; *C.A.* **31**, 5382 (1937). (10) Kalle and Co., Ger. 343,147, Oct. 28, 1921; *Cent.* **1922**, II 144.

3:3750 2,6-DICHLOROBENZOQUINONE-1,4
(*m*-Dichlorobenzoquinone)



$C_6H_2O_2Cl_2$ Beil. VII - 633
VII$_1$-(347)

M.P.	121° cor.	(1)
	121°	(2)
	120.5°	(3)
	120°	(4) (5) (6) (9) (14) (17)
	120–121°	(7) (8)
	119°	(12)

[*See also* 2,6-*dichlorohydroquinone* (3:4600).]

Yellow cryst. from C_6H_6 or lgr.; yellow pr. from alc. or AcOH. — $\bar{C}$ is somewhat sol. boilg. aq. or cold alc.; eas. sol. hot alc.; sol. $CHCl_3$. — Sublimes far below m.p.; volatile

with steam. — $\bar{C}$ turns skin reddish brown. [For study of photochem. decompn. of alc. soln. see (43).]

[For prepn. of $\bar{C}$ from 2,6-dichlorohydroquinone (3:4600) with CrO_3 (7) or with excess aq. $FeCl_3$ soln. on *warming* (9) see indic. *refs.*; from 2,4,6-trichlorophenol (3:1673) on oxidn. with CrO_3 in AcOH at 30–40° (yields: 60% (3), 27% (10)) (2), with cold fumg. HNO_3 (25% yield (11)) (6), with mixt. of fumg. HNO_3 + conc. H_2SO_4 (12), with PbO_2 in AcOH or in C_6H_6 (10) or in alc. with HNO_2 (13) (14) cf. (10), see indic. refs. (note that in addn. to $\bar{C}$ the crude oxidn. prod. contains also 2-*chloro*-6-(2',4',6'-*trichlorophenoxy*)-benzoquinone-1,4, m.p. 134–135° (10), and 2,6-*bis*-(2',4',6'-trichlorophenoxy)benzoquinone-1,4, m.p. 245° (10), which resemble $\bar{C}$ in appearance, composition, and behavior); from 2,6-dichloro-4-fluorophenol (8) or its dimethyl ether (8) or from 2,6-dichloro-4-bromophenol (11) with ice-cold HNO_3 (D = 1.5) see indic. *refs.*; *from* 2,6-dichloro-4-nitrophenol [Beil. VI-241, VI$_1$-(122)] on htg. above its m.p. (125°) (15) or in small amt. with mixt. of fumg. HNO_3 + fumg. H_2SO_4 at ord. temp. (16); from 2,6-dichloro-4-aminophenol [Beil. XIII-512, XIII$_1$-(183)] by *oxidn. with* $K_2Cr_2O_7$ + H_2SO_4 *(90% yield (1)) (17) see indic. refs.*; *from* 3,5-dichloro-4-aminophenol [Beil. XIII-513] similarly see (18); *from* 2,6-dichloro-*p*-phenylenediamine [Beil. XIII-118, XIII$_1$-(37)] by oxidn. with dichromate see (19) (10); from 2,6-dichloro-4-bromophenol bromide (4) or from "2,4,6-trichlorophenol bromide" (2,4,6-trichloro-6-bromocyclohexadiene-1,4-one-3) [Beil. VII-145] (5) with cold fumg. HNO_3 see *indic. refs.*; *from* 2,6-dichlorobenzoquinone-1,4-(2,4-dinitroanil)-4 [Beil. XII-754] on hydrolysis with dil. H_2SO_4 in s.t. at 200° see (20).]

[For study of bactericidal value of $\bar{C}$ see (21); for use as vulcanization accelerator see (22); for condensation with β-naphthylamine and use of prods. as intermediates in prepn. of *sulfur dyes see* (23); *for condensation with various amines to yield corresp. mono- and* diarylaminoquinones see (24); for condensation with various aminophenols and use of prods. in prepn. of oxazine dyes see (25); for condensation of $\bar{C}$ with o-aminoaryl mercaptans and use in prepn. of vat dyes see (26); for reactn. with $Na_2S_2O_3$ + AcOH in prepn. of sulfur *dyes see* (40).]

$\bar{C}$ on reductn. with aq. SO_2 gives (80% yield (3)) (27) (1) 2,6-dichlorohydroquinone (3:4600) (note, however, that $\bar{C}$ in dil. aq. NaOH under N_2 with SO_2 is in part reduced to 2,6-dichlorohydroquinone (3:4600) and in part sulfonated to mono- and disulfonic acids of $\bar{C}$ (28)). — [For studies of the oxidn.-reductn. potential of system $\bar{C}$ + 2,6-dichlorohydroquinone see (3) (29) (30) (42).] — [$\bar{C}$ forms with 2,6-dichlorohydroquinone the corresp. quinhydrone, brown prismatic ndls., m.p. 135° (31), but does so less readily than the benzoquinone-1,4/hydroquinone system (3); *note that this same quinhydrone is obtd.* (36) from $\bar{C}$ + ord. hydroquinone (36).]

[$\bar{C}$ in $CHCl_3$ at low temp. does not react with Cl_2 but at ord. temps. gives (22) tetrachlorobenzoquinone-1,4 (chloranil) (3:4978). — $\bar{C}$ in AcOH at 15–20° gives (11) with 2 *moles* Br_2 2,6-*dichloro*-3,5-*dibromobenzoquinone*-1,4 [Beil. VII-642], m.p. 291° (11), accompanied by a little 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-642], m.p. 292° (11); but $\bar{C}$ in boilg. AcOH with 2 moles Br_2 gives exclusively the latter (11) cf. (19) (33).]

[$\bar{C}$ with conc. HCl gives on boilg. (34) both 2,3,5-trichlorobenzoquinone-1,4 (3:4072) and 2,3,5,6-tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).]

[$\bar{C}$ in cold alc. treated dropwise with 10% alc. KOH gives first a green soln. turning to brownish red and pptg. in poor yield (2) a potassium salt of 2-chloro-3,6-dihydroxybenzoquinone-1,4 [Beil. VIII-378]; $\bar{C}$ *in satd. alc. soln. at* 50–60° with conc. NH_4OH gives a purple soln. grad. turning brownish red and pptg. (20–25% yield (2)) 2-chloro-3,6-dihydroxybenzoquinone-1,4-diimide [Beil. VIII-379], bronze-colored lfts. from AcOH, subliming at 258–260° without melting.]

[$\bar{C}$ (1 pt.) in alc. (15–20 pts.) + conc. HCl (0.3–0.4 pts.) *treated with* aniline (0.25 pt.)

yields mainly (35) 2,6-dichloro-3-anilinobenzoquinone-1,4 [Beil. XIV-137], blue ndls. or lfts., m.p. 154° (35), and 2,6-dichlorohydroquinone (3:4600) accompanied by small amts. of 2-chloro-3,6-dianilinobenzoquinone-1,4 (see below); C̃ in either alc. or AcOH with excess *aniline yields* (35) *2-chloro-3,6-dianilinobenzoquinone-1,4* [Beil. XIV-143], brown lfts. from AcOH, m.p. 262° (35), and 2,6-dichlorohydroquinone (3:4600).] — [Note that C̃ with sulfanilic acid behaves similarly: e g., C̃ with 2 moles sulfanilic acid in aq. (best in pres. of NaOAc) yields (37) 2-chloro-3,6-*bis*-(*p*-sulfoanilino)benzoquinone-1,4 together with 2,6-dichlorohydroquinone (3:4600); in aq. alc., however, 2,6-dichloro-3-(*p*-sulfoanilino)benzoquinone is also formed (37).]

[C̃ with $NH_2OH.HCl$ in alc. yields (38) 2,6-dichlorobenzoquinone-1,4-monoxime-4, pale yel. lfts. from dil. alc., m.p. 140° (38), which with cold conc. HNO_3 oxidizes to 2,6-dichloro-4-nitrophenol [Beil. VI-241], colorless ndls. from aq., lfts. from AcOH, tbls. from ether, *m.p. 125° dec.; note that no dioxime can be formed.*]

[C̃ with semicarbazide HCl in cold dil. alc. gives (39) 2,6-dichlorobenzoquinone-1,4-*semicarbazone-4, in red or yel. forms acc. to conditions, but both of m.p. 218° dec. (39)*; note that no *bis*-semicarbazone can be formed.]

[C̃ with 20% soln. of triphenylphosphine in $CHCl_3$ gives an orange-red, red, or brown color (41) (also shown by trichlorobenzoquinone and by chloranil); for other limitations and details see (41).]

3:3750 (1) van Erp, *Ber.* **58**, 664–665 (1925). (2) Kehrmann, Tiesler, *J. prakt. Chem.* (2) **40**, 480–486 (1889). (3) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2202–2204 (1923). (4) Kohn, Sussmann, *Monatsh.* **46**, 586 (1925). (5) Kohn, Rabinowitsch, *Monatsh.* **48**, 353 (1927). (6) Faust, *Ann.* **149**, 153–155 (1869). (7) Den Hollander, *Rec. trav. chim.* **39**, 481–482 (1920). (8) Hodgson, Nixon, *J. Chem. Soc.* **1930**, 1868–1869. (9) Dakin, *Am. Chem. J.* **42**, 491 (1909). (10) Hunter, Morse, *J. Am. Chem. Soc.* **48**, 1615–1624 (1926).

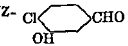
(11) Ling, *J. Chem. Soc.* **61**, 559–560, 566–567, 576–578, 580–581 (1892). (12) Guareschi, Daccomo, *Ber.* **18**, 1170 (1885). (13) Weselsky, *Ber.* **3**, 646–647 (1870). (14) Lampert, *J.* … *Ber.* **7**, 926 (1874). (16) Armstrong, *J.* … 14–15 (1886). (18) Bargellini, Leone, … (19) Levy, *Ber.* **16**, 1445–1447 (1883).

(21) Morgan, Cooper, *J. Soc. Chem. Ind.* **43**-T, 352–354 (1924). (22) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, I 3133. (23) Thiess, Maennchen (to I.G.), *Ger.* 507,833, *Sept. 20, 1930; Cent.* **1930**, *II 2839.* (24) Becke, *W. Suida, H. Suida, Ger.* …

(1934).

(31) Ling, Baker, *J. Chem. Soc.* **63**, 1321–1322 (1893). (32) Oliveri-Tortorici, *Gazz. chim. ital.* **27**, II 585–586 (1897). (33) Hantzsch, Schniter, *Ber.* **20**, 2279–2282 (1887). (34) Levy, Schultz, *Ann.* **210**, 153 (1881). (35) Niemeyer, *Ann.* **228**, 334–337 (1885). (36) Siegmund, *J. prakt. Chem.* (2) **92**, 361–362 (1915). (37) H. Suida, W. Suida, *Ann.* **416**, 136–142 (1918). … (1913).

Soc. **49**, 293–297 (1927).

3:3780 **4-CHLORO-3-HYDROXYBENZALDEHYDE** 

$C_7H_5O_2Cl$ Beil. S.N. 746

M.P. 121° (1) (2)

Colorless ndls. (1).

[For prepn. of C̃ from *m*-hydroxybenzaldehyde (1:0055) via 4-nitro-3-hydroxybenzaldehyde, reduction to amino cpd., and use of appropriate diazo reactn. see (1).]

C̃ in 50% AcOH mononitrated as specified (2) gives mainly 4-chloro-2-nitro-3-hydroxybenzaldehyde, spar. sol. in hot $CHCl_3$, colorless pr. from AcOH, m.p. 175° (2) (3). [Note that this statement takes account of a very important correction (3).] [This 4-chloro-2 nitro-3-hydroxybenzaldehyde yields the following derivs.: *p*-nitrophenylhydrazone, deep maroon ndls. from hot AcOH, m.p. 275–276° dec.; semicarbazone, lt. or. ndls. from alc., m p. 265–266° dec. (2)]

C̃ in aq. contg $NaHCO_3$ treated with $(CH_3)_2SO_4$ yields (1) 4-chloro-3-methoxybenzaldehyde, m.p. 52° (1). [This prod. depresses m.p. of corresp. methyl ether of the isomeric 2-chloro-3-hydroxybenzaldehyde (3:4085), m p. 56–57° (1); on keeping it acquires a beautiful silver-gray color (1); it yields an oxime, colorless ndls., m.p. 98–99°, and a *p*-nitrophenylhydrazone, old-gold ndls., m.p. 251° (1).]

Ⓓ **4-Chloro-3-hydroxybenzaldoxime:** colorless ndls. of hydrate, dec. 106–110° from dil. alc.; anhydrous oxime, m.p. 126° (1).

—— **4-Chloro-3-hydroxybenzaldehyde phenylhydrazone:** unrecorded.

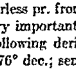
Ⓓ **4-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** violet-red ndls. from dil. alc , m.p 226–227° (1).

—— **4-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.

Ⓓ **4-Chloro-3-hydroxybenzaldehyde semicarbazone:** pale yel. ndls., m p. 238–239° (1).

3:3780 (1) Hodgson, Beard, *J. Chem. Soc.* **1926**, 150–154. (2) Hodgson, Beard, *J. Chem. Soc.* **1926**, 2033–2034. (3) Hodgson, Beard, *J. Chem. Soc.* **1927**, 2377–2378.

3:3810 7-CHLORONAPHTHOL-1



$C_{10}H_7OCl$ Beil. VI - 612, VI_1—, VI_2—

M.P. 123° (1)

Ndls. from aq or CS_2; spar. sol. aq. — C̃ has odor suggesting that of iodoform.

[For prepn. of C̃ from γ-(*p*-chlorophenyl)paraconic acid [Beil. XVIII-421] by distn. see (1).]

C̃ dis. in aq alk. from which it is repptd. by CO_2; the alk. soln. of C̃ couples with diazonium salts yielding azo dyestuffs (1).

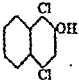
C̃ with aq $FeCl_3$ gives a yellowish white ppt. which on stdg. assumes a pronounced violet color (1)

C̃ (1 mole) with PkOH (1 mole) in $CHCl_3$ yields an addn. cpd., C̃.PkOH, or.-red. ndls. from hot $CHCl_3$, m.p 139° (1).

—— **7-Chloro-1-naphthyl acetate:** oil.

3:3810 (1) Erdmann, Kirchhoff, *Ann.* **247**, 374–375 (1888).

3:3840 1,4-DICHLORONAPHTHOL-2



$C_{10}H_6OCl_2$ Beil. VI - 650, VI_1—, VI_2—

M.P. 123–124° (1)
122–123° (2)
121° (3)

Ndls. from lgr ; eas sol alc., ether, or AcOH.

[For prepn. of C̃ from 1,1-dichloro-2-keto-1,2-dihydronaphthalene, m.p. 54° (2), 48–50°

(3) (itself prepd. from naphthol-2 (1:1540) in AcOH + NaOAc soln. with Cl_2 (2) (3)), by shaking with satd. soln. of HCl gas in AcOH for 2–3 min. (2) (3) see indic. refs.; from 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] by partial reduction with $SnCl_2$ in AcOH (poor yield) see (1); from 1-chloronaphthol-2 (3:1700) with SO_2Cl_2 at ord. temp. (4) (note that this prepn. undoubtedly involves intermediate formn. of 1,1-dichloro-2-keto-1,2-dihydronaphthalene (above) (2)) see indic. refs.; from 1,4,5-trichloronaphthol-2 [Beil. VI-650] by partial reduction with Na/Hg see (4).]

[C̄ in AcOH with Cl_2 gives (1) 1,1,4-trichloro-2-keto-1,2-dihydronaphthalene [Beil. VII-386], m.p. 86–87°, together with other oily by-products.]

C̄ with $SnCl_2$/AcOH/HCl in s.t. at 100° for 8 hrs. gives (72% yield (2)) (3) 4-chloronaphthol-2 (3:3045), m.p. 103–104°.

C̄ in AcOH mixed with conc. HNO_3 ($D = 1.42$) and cautiously warmed until the liq. shows intense red color, then poured into aq., yields (1) 4-chloro-3-nitronaphthoquinone-1,2 [Beil. VII-724], red ndls. from AcOH, m.p. 184° (1).

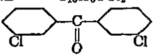
C̄ with aq. alc. Na_2SO_3 boiled 72 hrs. gives in poor yield (2) 4-chloronaphthol-2-sulfonic acid-1, cryst. from aq. with ½ H_2O (not lost at 100° in vac.); note that this prod. on hydrolysis with H_2SO_4 gives (91% *yield* (2)) *4-chloronaphthol-2 (3:3045), m.p. 103–104°.*

Ⓓ **1,4-Dichloro-2-naphthyl acetate:** m.p. 90–91° (1). [From C̄ with AcCl (1).]

3:3840 (1) [illegible] (2) Burton, *J. Chem. Soc.* **1945**, 280–283. [illegible] (1930). (4) Armstrong, Rossiter, *Chem.* [illegible]

3:3860 3,3′-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. S.N. 652

(Di-(*m*-chlorophenyl) ketone)



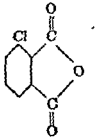
M.P. 123.8–124.9° (1) B.P. 160–166° at 2 mm. (1)

[For prepn. of C̄ from *m*-chlorobromobenzene [Beil. V-209, V_1-(115), V_2-(161)] (2) via conversion to *m*-chlorophenyl MgBr (cf. (3)) and reaction with *m*-chlorobenzonitrile [Beil. IX-339] (4), followed by hydrolysis (77% *yield*), see (1).]

Ⓓ **3,3′-Dichlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 235–238° (1).

3:3860 (1) Haller, Bartlett, Drake, Newmann, Cristol, et al., *J. Am. Chem. Soc.* **67**, 1600–1602 (1945). (2) Hartwell, *Org. Syntheses* **24**, 22–24 (Note 5) (1944). (3) Hein, Retter, *Ber.* **71**, 1968 (1938). (4) Korczynski, Fandrich, *Compt. rend.* **183**, 421–423 (1926); *Cent.* **1926**, II 1853; *C.A.* **21**, 77 (1927).

3:3900 3-CHLOROPHTHALIC ANHYDRIDE



$C_8H_3O_3Cl$ Beil. XVII - 482 $XVII_1$—

M.P. 126° (1)
124.5–125.5° (2)
123° (3)
122° (4) (5)

[*See also 3-chlorophthalic acid* (3:4820).]

[For prepn. of C̄ from 3-chlorophthalic acid (3:4820) by *distn.* see *(4) (2)*; from 3-nitrophthalic anhydride [Beil. XVII-486, $XVII_1$-(256)] by htg. with PCl_5 in s.t. 6 hrs. at 175° (5) or 9 hrs. at 220° (60% yield (1)) or with Cl_2 at 240° (6) see indic. refs.; from phthalic anhydride (1:0725) with Cl_2 at 240° in pres. of Fe or Fe salts see (7).]

[C̄ with Cl_2 in fumg. H_2SO_4 in pres. of I_2 gives (8) a mixt. contg. 3 pts. 3,6-dichlorophthalic anhydride (3:4860), m.p. 194° cor., and 1 pt. 3,4-dichlorophthalic anhydride (3:3695), m.p. 120–121°, b.p. 329°.]

[The neutral dimethyl and diethyl esters corresp. to C̄ are unreported; ethyl hydrogen 3-chlorophthalate has m.p. *118–119° (3).*]

[C̄ with PCl_5 (3) or with $SOCl_2$ + $ZnCl_2$ in s.t. at 200–240° (9) yields 3-chlorophthaloyl (di)chloride, b.p. 169–171° at 16 mm. (3).]

C̄ with urea on fusion at 170° gives (3) 3-chlorophthalimide, cryst. from AcOH, m.p. 233° (3), 236° (15) — C̄ with 1 mole aniline htd. at 200–220° until no more steam is evolved (14) or C̄ with 1 mole aniline in boilg. AcOH (14) gives quant. yield 3-chlorophthalanil (*N*-phenyl-3-chlorophthalimide), pale cream-colored ndls. from AcOH, m.p. 189–190° (14); C̄ similarly treated with *p*-toluidine gives (80–90% yield (14)) *N*-(*p*-tolyl)-3-chlorophthalimide, colorless ndls. from AcOH, m.p. 160.5° (14).

[C̄ with pyrocatechol (1:1520) + $AlCl_3$ + NaCl htd. at 130–138° gives (10) an intermediate prod. (presumably 3-chloro-2-(*o,m*-dihydroxybenzoyl)benzoic acid), yel. cryst. from AcOH, m.p. 187° (10), which with conc. H_2SO_4 yields (10) 8-chloro-1,2-dihydroxyanthraquinone (5-chlorohystazarin), yel. cryst. from pyridine, m.p. 187° (diacetate, m.p. 193° (10)). — C̄ with hydroquinone (1:1590) + $AlCl_3$ + NaCl htd. at 200–220° for 40–50 min. yields (11) 8-chloro-1,4-dihydroxyanthraquinone (5-chloroquinizarin), red cryst. from xylene, m.p. 213° (diacetate, m.p. 205°, dimethyl ether, m.p. 208° (11)).]

[C̄ with C_6H_6 + $AlCl_3$ yields (12) 6-(3?)-chloro-2-(benzoyl)benzoic acid, m.p. 233.5°, which with conc. H_2SO_4 for 4 hrs. at 95° gives (59% yield (12)) 1-chloroanthraquinone (3:4180), m.p. 162° (12) — C̄ with *p*-xylene + $AlCl_3$ gives (81% yield (13)) 6-(3?)-chloro-2-(2,5-dimethylbenzoyl)benzoic acid, pr. from AcOH, m.p. 215°, which on warming with 9 pts. fumg. H_2SO_4 (10% SO_3) gives (96% yield (13)) 1-chloro-5,8-dimethylanthraquinone, yel. ndls. from AcOH, m.p. 186°.]

C̄ on boilg. with dil. HCl (1) or C̄ on saponification with standard alk. (Sap. Eq. = 91.3) followed by acidifn. gives 3-chlorophthalic acid (3:4820) q.v.

3:3900 (1) Smith, *J. Chem. Soc.* **1933**, 1643–1644. (2) Guareschi, *Gazz. chim. ital.* **17**, 122 (1887). (3) von Braun, Larbig, Kredel, *Ber.* **56**, 2335 (1923). (4) Kröger, *Ber.* **18**, 1759 (1885). (5) Bogert, Boroschek, *J. Am. Chem. Soc.* **23**, 751–752 (1901). (6) Imperial Chem. Ind., Ltd., Shaw, Thomas, Brit. 357,165, Oct. 15, 1931; *Cent.* **1931**, II 3663. (7) Dvornikoff (to Monsanto

Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* **1936**, I 2830; *C.A.* **30**, 1394 (1936). (8) Villiger, *Ber.* **42**, 3549 (1909). (9) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; *Cent.* **1934**, II 333. (10) Waldmann (to I.G.), Ger. 642,719, March 12, 1937; *Cent.* **1937**, I 5048–5049; *C.A.* **31**, 6261 (1937).

(11) Waldmann, *J. prakt. Chem.* (2) **130**, 100 (1931). (12) Dougherty, Gleason, *J. Am. Chem. Soc.* **52**, 1024–1027 (1930). (13) Mayer, Heil, *Ber.* **55**, 2163 (1922). (14) Marriott, Robinson, *J. Chem. Soc.* **1939**, 136–137. (15) Drew, Pearman, *J. Chem. Soc.* **1937**, 31.

3:3925 7-CHLORONAPHTHOL-2

$C_{10}H_7OCl$ Beil. VI - 649
VI_1—
VI_2-(603)

M.P. 126.5° (1)

White lfts. from lgr.

[For prepn. of C̄ from 7-hydrazinonaphthol-2 [Beil. XV-613] by treatment of its soln. in dil. HCl with $CuSO_4$ (19% yield) see (1).]

[C̄ (as sodium salt) treated with CO_2 at 230–250° and 45 atm. press. yields (2) 7-chloro-2-hydroxynaphthoic acid-3, yellowish lfts. from AcOH, m.p. 277–278° (2).]

Ⓓ 7-Chloro-2-naphthyl acetate: lfts. from toluene, m.p. 104.5° (1). [From C̄ on refluxing with acetyl chloride (1).]

3:3925 (1) Fransen, Deibel, *J. prakt. Chem.* (2) **78**, 154 (1878). (2) Lange, Luce, Jacobs (to I.G.), Ger. 564,128, Nov. 14, 1932; *Cent.* **1933**, II 446.

3:3934 *p*-PHENYLPHENACYL CHLORIDE
(ω-Chloro-*p*-phenylacetophenone;
chloromethyl *p*-xenyl ketone;
4-(chloroacetyl)biphenyl)

$C_{14}H_{11}OCl$ Beil. VII - 443
VII_1—

M.P. 126–127° (1)
122–123° (2) (3)

Pale yel. ndls. from dil. alc.

[For prepn. of C̄ from biphenyl (1:7175) with chloroacetyl *chloride* (3:5235) + $AlCl_3$ (41% yield (2)) (3), or with chloroacetic acid anhydride (3:0730) + $AlCl_3$ (77% yield (2)), see indic. refs.]

[C̄ with chloroacetyl chloride (3:5235) + $AlCl_3$ gives (52% yield (2)) 4,4′-*bis*-(chloroacetyl)biphenyl, ndls. from di-*n*-propyl ketone or cyclohexanone, m.p. 228–229° (2), 226–227° (4); note that this prod. with excess piperidine yields (4) 4,4′-*bis*-(piperidinoacetyl)biphenyl, brownish yel. pdr. from acetone, m.p. 143–144° (4).]

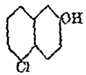
[C̄ with piperidine has not been directly reported but should yield 4-(piperidinoacetyl)biphenyl, ndls. from abs. alc., m.p. 93–94° (4), as has been demonstrated for the analogous p-phenylphenacyl *bromide*.]

C̄ with salts of acids should yield the corresp. *p*-phenylphenacyl esters (for table of examples see Vol. I, p. 652) although the usual reagt. for this purpose is the more common [illegible]

[illegible]° is oxidized (3) to *p*-phenylbenzoic acid [illegible]).

3:3934 (1) Eastman Kodak Co., List No. 34 (1944). (2) Silver, Lowy, *J. Am. Chem. Soc.* **56**, 2429–2430 (1934). (3) Collet, *Bull. soc. chim.* (3) **17**, 510 (1897). (4) Carpenter, Turner, *J. Chem. Soc.* **1934**, 872.

3:3945 5-CHLORONAPHTHOL-2



$C_{10}H_7OCl$ Beil. VI - 649
VI₁—
VI₂—

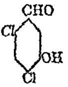
M.P. 128° u.c. (1)

Ndls; sol. alc., AcOH, C_6H_6, CS_2. — Sublimes; *volatile with steam.*

[For prepn. of C̄ from salts of 2-hydroxynaphthalenesulfonic acid-5 [Beil. XI-282] by htg. with PCl_5, then distilling with steam, see (1).]

3:3945 (1) Claus, *J. prakt. Chem.* (2) 39, 317 (1889).

3:3952 4,6-DICHLORO-3-HYDROXY-BENZALDEHYDE



$C_7H_4O_2Cl_2$ Beil. VIII —
VIII₁-(526)

M.P. 130° (1)
129° (2)

Fairly eas. sol. hot aq.; eas. sol. C_6H_6, alc.; insol. lgr. — *Volatile with steam.* C̄ has very pronounced sternutatory props and also attacks moist skin producing *painful blisters* (2).

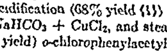
[For prepn. of C̄ from 4,6-dichloro-3-methylphenol (3:1745) via conv. to *bis*-(4,6-dichloro-3-methylphenyl) carbonate, chlorination of latter, and subsequent alk. hydrol. of the chlorination prod. see (1); for formn. (in small amt. together with much 2,6 isomer) from 6-chloro-3-hydroxybenzaldehyde (3:3350) or from *m*-hydroxybenzaldehyde (1:0055) in AcOH with Cl_2 see (2).]

C̄ in 4 pts. AcOH + 1 pt. aq. treated grad. with 1 pt. conc. HNO_3 ($D = 1.4$) yields (1) 4,6-dichloro-2-nitro-3-hydroxybenzaldehyde, m.p. 157° (1); this prod. with acetone and alk. yields (1) the corresp. indigoid, viz., 4,4,6,6-tetrachloro-7,7-dihydroxyindigo.

—— 4,6-Dichloro-3-methoxybenzaldehyde: ndls. from C_6H_6, m.p. 117° (1).

3:3952 (1) Friedländer, Schenck, *Ber.* 47, 3048, 3051 (1914). (2) Hodgson, Beard, *J. Chem. Soc.* 1926, 148–149, 152.

3:3956 *o*-CHLOROPHENYLPROPIOLIC ACID $C_9H_5O_2Cl$ Beil. S.N. 950



M.P. 131–132° (1) (2)
131° (3)

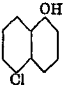
Cryst. from 50% AcOH or C_6H_6.

[For prepn. of C̄ from *o*-chlorobenzaldehyde (3:6410) by conversion through *o*-chlorocinnamic acid to ethyl *o*-chlorocinnamate, thence by addn. of Br_2 to give ethyl β-(*o*-chlorophenyl)-α,β-dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (68% yield (1)) (2) cf. (3), see indic. refs.]

C̄ suspended in aq., treated with $NaHCO_3$ + $CuCl_2$, and steam-distilled (1) or C̄ with $Cu(OAc)_2$ (2) loses CO_2 giving (66% yield) *o*-chlorophenylacetylene (3:9497).

3:3956 (1) Bergmann, Bondi, *Ber.* 66, 282–283 (1933). (2) Otto, *J. Am. Chem. Soc.* 56, 1393–1394 (1934). (3) Wilson, Wenzke, *J. Am. Chem. Soc.* 57, 1265–1267 (1935).

3:3960 5-CHLORONAPHTHOL-1



$C_{10}H_7OCl$ Beil. VI - 612
VI₁—
VI₂—

M.P. 131.5° (1)

Ndls. from aq., lfts. from CS_2; spar. sol. aq. — C̄ has characteristic odor.

[For prepn. of C̄ from γ-(2-chlorophenyl)paraconic acid [Beil. XVIII-421] on rapid distn. see (1).]

[For condensation of C̄ with subst. isatin chlorides in prepn. of indigoid dyes see (2).]

C̄ dis. in aq. alk. and this soln. couples (1) with diazonium salts yielding azo dyestuffs

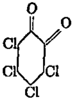
C̄ with aq. $FeCl_3$ gives a yellowish-white ppt. unchanged on stdg.; C̄ with $Ca(OCl)_2$ soln. gives a pale violet ppt. (1).

C̄ (1 mole) in $CHCl_3$ on mixing with PkOH (1 mole) in $CHCl_3$ gives (1) ppt. of addn. cpd., C̄.PkOH, orange ndls. from hot $CHCl_3$, m.p. 160° (1).

Ⓓ **5-Chloro-1-naphthyl acetate:** lfts. from alc., m.p. 53° (1). [From C̄ on protracted boilg. with AcCl (1).]

3:3960 (1) Erdmann, Kirchhoff, *Ann.* **247**, 372–374 (1888). (2) I.G., Brit. 318,107, Oct. 23, 1929; *Cent.* **1930**, I 1383.

3:3965 TETRACHLOROBENZO-QUINONE-1,2
(Tetrachloro-*o*-quinone)



$C_6O_2Cl_4$ Beil. VII - 602
VII₁-(338)

M.P. 133° (1)
131–132° (2)
130° (4) (7)
129–130° (3)
129° (11)

[*See also tetrachloropyrocatechol* (3:4875).]

Red cryst. pdr. (1), cryst. from dil. AcOH (2).

[For prepn. of C̄ from tetrachloropyrocatechol (3:1520) by oxidn. with fumg. HNO_3 in AcOH (81% yield (1)) (2) (3) (4) (5) (6) see indic. refs.; from pyrocatechol (1:1520) (2) (3) or pyrocatecholsulfonic acid (7) with Cl_2 in AcOH see indic. refs.; from tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) (8) or from tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) (8) by oxidn. with HNO_3 see indic. refs.]

[C̄ adds 1 mole Cl_2 yielding (9) hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] q.v. which on reduction with $SnCl_2$ in AcOH (3) gives tetrachloropyrocatechol *(3:4875).*]

[C̄ with PCl_5 (2 moles) htd. in s.t. at 200–210° for ½ hr. gives (10) hexachlorobenzene (3:4939) and other products.]

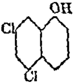
[For complex behavior of C̄ on htg. with aq., with cold alcs., or with aniline see Beil. VII-602, VII₁-(338).]

C̄ forms addn. cpds. with many hydrocarbons [e.g., C̄ with benzene gives C̄.$3C_6H_6$, m.p. 37–42° (11); C̄ with toluene gives C̄.C_7H_8, m.p. 45–50° (11); C̄ with hexamethylbenzene (1:7265) gives C̄.$C_{12}H_{18}$, greenish black ndls. from AcOH, m.p. 140–143° (11).]

C̄ with equiv. tetrachloropyrocatechol (3:4875) in least possible hot $CHCl_3$ gives on

cooling the corresp. quinhydrone (6). — [For study of oxidn.-reductn. potential of system C̄/tetrachloropyrocatechol see (4) (5).]

3:3965 (1) Jackson, MacLaurin, *Am Chem. J.* **37**, 11–12 (1907). (2) Zincke, *Ber.* **20**, 1779 (1887). (3) Zincke, Küster, *Ber.* **21**, 2729–2730 (1888). (4) Conant, Fieser, *J. Am. Chem. Soc* **46**, 1873, 1875 (1924). (5) Kvalnes, *J. Am. Chem. Soc.* **56**, 2487–2489 (1934). (6) Jackson, Carleton, *Am. Chem. J.* **39**, 497 (1909). (7) Datta, Bhoumik, *J. Am. Chem. Soc.* **43**, 313 (1921). (8) Cousin, *Compt. rend.* **129**, 967 (1899). (9) Zincke, Küster, *Ber.* **22**, 487 (1889). (10) Zincke, Küster, *Ber.* **24**, 927–928 (1891).
(11) Pfeiffer, *Ann* **412**, 294–296 (1916).

3:3985 5,7-DICHLORONAPHTHOL-1  $C_{10}H_6OCl_2$ Beil. VI - 612 VI_1—

M.P. 132° (1) (2)

Pale yel. pr. (from CS_2) (1) (2). — Somewhat sol. hot aq.

[For prepn from γ-(2,4-dichlorophenyl)paraconic acid [Beil. XVIII-421] by distn. see (2).]

C̄ with $FeCl_3$ gives a white ppt. which on htg. with excess reagt. colors violet (2).

C̄ in dil. alk. soln. couples with diazotized naphthionic ac. (1-aminonaphthalenesulfonic acid-4) giving intense purple color (2).

C̄ on distn. with Zn dust yields naphthalene (1:7200) (2) (1).

Ⓓ 5,7-Dichloro-1-naphthyl acetate: from C̄ on protracted refluxing with 4 pts. AcCl; pr. (from $CHCl_3$ + lgr.), m.p. 110° (2).

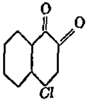
3:3985 (1) Erdmann, Schwechten, *Ber.* **21**, 3444 (1888). (2) Erdmann, Schwechten, *Ann.* **275**, 284–285 (1893).

CHAPTER X

DIVISION A. SOLIDS

(3:4000–3:4499)

3:4000 4-CHLORONAPHTHO-QUINONE-1,2



$C_{10}H_5O_2Cl$ Beil. S.N. 674

M.P. 132–136° dec. (1)
[188° (2) see text]

Orange-red ndls. from C_6H_6 by addn. of lgr.; C̄ could not be further purified by recrystallization since some decompn. always occurred (1).

[For prepn. of C̄ from 1,4-dichloronaphthol-2 (3:3840) by conversion (59% *yield*) with HNO_3 in AcOH to 1,4-dichloro-1-nitro-2-keto-dihydronaphthalene, followed by subsequent elimination of NOCl by boiling with C_6H_6 (80% yield), see (1). — Note that the prod. of m.p. 188°, maroon ndls. from alc., obtd. (2) from 4-chloro-1,2-diaminonaphthalene (4-chloronaphthylenediamine-1,2) by air oxidn., is regarded as C̄; this discrepancy is unexplained.]

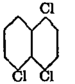
C̄ on reductive acetylation with Ac_2O + NaOAc + Zn dust loses its halogen atom giving (60% yield (1)) 1,2,4-triacetoxynaphthalene [Beil. VI-1133], m.p. 134–135° (1).

[C̄ with 2,3-dimethylbutadiene (1:8050) in specially purified $CHCl_3$ in s.t. at 100° in dark for 72 hrs. undergoes a Diels-Alder type addition only very slowly (1); no intermediate addn. prod. could be isolated (*difference from the isomeric 3-chloronaphthoquinone-1,2* (3:4704)), but on stdg. the soln. slowly deposits (15% yield (1)) 2,3-dimethylphenanthraquinone, m.p. 237–238° u.c.; 242–243° cor. (1).]

—— 4-Chloronaphthoquinone-1,2-oxime-2 (4-chloro-2-nitrosonaphthol-1) [Beil. VII_1-(385)]: pale yel. ndls., m.p. 157°. [Prepd. indirectly.]

3:4000 (1) Fieser, Dunn, *J. Am. Chem. Soc.* **59**, 1019–1020 (1937). (2) Hodgson, Elliott, *J. Chem. Soc.* **1935**, 1853.

3:4005 1,4,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ Beil. V - 545
V_1—
V_2-(446)

M.P. 133° (1)
131° (2) (3) (4)
129° u.c. (3)

Ndls. from alc. in which C̄ is spar. sol. — Volatile with superheated (3) steam.

[For formn. of C̄ from sodium 1,5-dinitronaphthalenesulfonate-4 (1) with HCl + $NaClO_3$

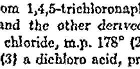
see (1); for prepn. of C̄ from 1,5-dichloro-4-nitronaphthalene [Beil. V-550] (3), from 1,4-dichloro-5-nitronaphthalene [Beil. V-556, V_1-(264)] (4) (3), from 4-chloro-1,5-dinitronaphthalene [Beil. V-561] (3), *from 1-chloro-4,5-dinitronaphthalene* [Beil. V-561] (3), from 4,5-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 4-chloro-5-nitronaphthalenesulfonyl chloride-1 [Beil. XI-169] (6), from 1-chloro-5-nitronaphthalenesulfonyl chloride-4 [Beil XI-170] (6), from 5-chloro-4-nitronaphthalenesulfonyl chloride-1 [Beil. XI-170] (6), from 1-chloro-4-nitronaphthalenesulfonyl chloride-5 [Beil. XI-170] (6), or from 4-chloronaphthalene-1,5-*bis*-(sulfonyl chloride) [Beil. XI-213] (7) (2), each with PCl_5 as directed, see indic. refs.]

[C̄ *treated* with $ClSO_3H$ in CS_2 and reactn. prod. conv. to salts as directed (2) yields a mixt. of two sulfonates, viz., one derived from 1,4,5-trichloronaphthalenesulfonic acid-7 (*corresp. sulfonyl chloride, m.p. 118° (2)*) and the other *derived from 1,4,5-trichloro*naphthalenesulfonic acid-X (corresp. sulfonyl chloride, m.p. 178° (2)).]

[C̄ on oxidn. with dil. HNO_3 in s t. yields (3) a dichloro acid, presumably 3,6-dichlorophthalic acid (3:4870).]

3:4005 ... (1922). (2) Turner, Wynne, *J. Chem.* ... 1187, 1733–1734 (1876) (4) Widman, *Bull.* ... (5) Armstrong, Wynne, *Chem. News* 61, 273 (1890). (6) Cleve, ... 11, 398 (1893). (7) Armstrong, Wynne, *Chem. News* 62, 163 (1890).

3:4020 3-CHLORO-2,2,3-TRIMETHYLBUTANE $C_7H_{15}Cl$ Beil. I - 158
(*ter*-Butyl-dimethyl-carbinyl chloride) I_1-(59) I_2—



M.P. 136° (1)
133° (4)
129° in s.t. (2)
123° (3)

Colorless cryst with camphoraceous odor; extremely volatile and readily ...; insol. aq. and volatile with steam; purified by sublimation or crystn. from ...

[For prepn. of C̄ from 2,2,3-trimethylbutanol-3 (pentamethylethanol) [Beil. ... (207), I_2-(447)] (3) or its hydrate (1) with fumg. HCl (2) (3), *with PCl_5* ... (3 7065) (46% yield (4)) see indic. refs; from 2,2,3-trimethylbutane ... with *ter*-butyl chloride (3·7045) + $AlCl_3$ by shaking 30-45 ...

C̄ with alc $AgNO_3$ ppts. AgCl even in cold (3).

C̄ *with Mg in dry ether gives RMgCl; this upon oxidn. with* ... yields (2) 2,2,3-trimethylbutanol-2, m p. 80° (2).

C̄ converted to RMgCl and the latter treated with CO_2 ... acetic acid [Beil II_2-(150)], m p. 80° ...

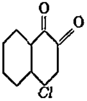
3:4020 ... (2) ... Soc. 66, 1533, 1537 (194...

CHAPTER X

DIVISION A. SOLIDS

(3:4000–3:4499)

3:4000 4-CHLORONAPHTHO-QUINONE-1,2



$C_{10}H_5O_2Cl$ **Beil. S.N. 674**

M.P. 132–136° dec. (1)
[188° (2) see text]

Orange-red ndls. from C_6H_6 by addn. of lgr.; C̄ could not be further purified by recrystallization since some decompn. always occurred (1).

[For prepn. of C̄ from 1,4-dichloronaphthol-2 (3:3840) by conversion (59% yield) with HNO_3 in AcOH to 1,4-dichloro-1-nitro-2-keto-dihydronaphthalene, followed by subsequent elimination of NOCl by boiling with C_6H_6 (80% yield), see (1). — Note that the prod. of m.p. 188°, maroon ndls. from alc., obtd. (2) from 4-chloro-1,2-diaminonaphthalene (4-chloronaphthylenediamine-1,2) by air oxidn., is regarded as C̄; this discrepancy is unexplained.]

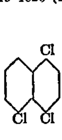
C̄ on reductive acetylation with Ac_2O + NaOAc + Zn dust loses its halogen atom giving (60% yield (1)) 1,2,4-triacetoxynaphthalene [Beil. VI-1133], m.p. 134–135° (1).

[C̄ with 2,3-dimethylbutadiene (1:8050) in specially purified $CHCl_3$ in s.t. at 100° in *dark for 72 hrs. undergoes a Diels-Alder type addition only very slowly (1); no intermediate* addn. prod. could be isolated (difference from the isomeric 3-chloronaphthoquinone-1,2 (3:4704)), but on stdg. the soln. slowly deposits (15% yield (1)) 2,3-dimethylphenanthraquinone, m.p. 237–238° u.c.; 242–243° cor. (1).]

—— 4-Chloronaphthoquinone-1,2-oxime-2 (4-chloro-2-nitrosonaphthol-1) [Beil. VII₁-(385)]: pale yel. ndls., m.p. 157°. [Prepd. indirectly.]

3:4000 (1) Fieser, Dunn, *J. Am. Chem. Soc.* **59**, 1019–1020 (1937). (2) Hodgson, Elliott, *J. Chem. Soc.* **1935**, 1853.

3:4005 1,4,5-TRICHLORONAPHTHALENE



$C_{10}H_5Cl_3$ **Beil. V - 545**
V_1—
V_2-(446)

M.P. 133° (1)
131° (2) (3) (4)
129° u.c. (3)

Ndls. from alc. in which C̄ is spar. sol. — Volatile with superheated (3) steam.

[For formn. of C̄ from sodium 1,5-dinitronaphthalenesulfonate-4 (1) with HCl + $NaClO_3$

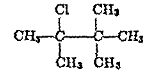
see (1); for prepn. of $\bar{C}$ from 1,5-dichloro-4-nitronaphthalene [Beil. V-556] (3), from 1,4-dichloro-5-nitronaphthalene [Beil. V-556, V_1-(264)] (4) (3), from 4-chloro-1,5-dinitronaphthalene [Beil. V-561] (3), from 1-chloro-4,5-dinitronaphthalene [Beil. V-561] (3), from 4,5-dichloronaphthalenesulfonyl chloride-1 [Beil. XI-162] (5), from 4-chloro-5-nitronaphthalenesulfonyl chloride-1 [Beil. XI-169] (6), from 1-chloro-5-nitronaphthalenesulfonyl chloride-4 [Beil. XI-170] (6), from 5-chloro-4-nitronaphthalenesulfonyl chloride-1 [Beil. XI-170] (6), from 1-chloro-4-nitronaphthalenesulfonyl chloride-5 [Beil. XI-170] (6), or from 4-chloronaphthalene-1,5-*bis*-(sulfonyl chloride) [Beil. XI-213] (7) (2), each with PCl_5 as directed, see indic. refs]

[$\bar{C}$ treated with $ClSO_3H$ in CS_2 and reactn. prod. conv. to salts as directed (2) yields a mixt. of two sulfonates, viz., one derived from 1,4,5-trichloronaphthalenesulfonic acid-7 (corresp sulfonyl chloride, m.p. 118° (2)) and the other derived from 1,4,5-trichloronaphthalenesulfonic acid-X (corresp. sulfonyl chloride, m p. 178° (2)).]

[$\bar{C}$ on oxidn. with dil. HNO_3 in s.t yields (3) a dichloro acid, presumably 3,6-dichlorophthalic acid (3:4870).]

3:4005 (1) Friedländer, Karamessinis, Schenk, *Ber.* **55**, 47 (1922). (2) Turner, Wynne, *J. Chem. Soc.* **1941**, 247, 254–255 (3) Atterberg, *Ber.* **9**, 1187, 1733–1734 (1876). (4) Widman, *Bull. soc. chim.* (2) **28**, 511 (1877). (5) Armstrong, Wynne, *Chem. News* **61**, 273 (1890). (6) Cleve, *Chem. Ztg.* **17**, 398 (1893) (7) Armstrong, Wynne, *Chem. News* **62**, 163 (1890).

3:4020 3-CHLORO-2,2,3-TRIMETHYLBUTANE $C_7H_{15}Cl$ **Beil. I - 158**
(*ter*-Butyl-dimethyl-carbinyl chloride) I_1-(59)
I_2—



M.P.	136°	(1)
	133°	(4)
	129° in s.t.	(2)
	123°	(3)

Colorless cryst with camphoraceous odor; extremely volatile and readily sublimes; insol. aq. and volatile with steam; purified by sublimation or cr[illegible] *rom boilg MeOH.*

[*For prepn. of $\bar{C}$ from 2,2,3-trimethylbutan*[illegible] *nol)* [*Beil. I-418, I_1-*(207), I_2-(447)] (3) or its hyd[illegible] Cl_5 (1) or with AcCl (3:7065) (46% [illegible] *riptane*") (1:8544) with *ter*-[illegible] *seconds* (16% yield) see (4)]

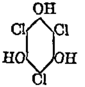
$\bar{C}$ with [illegible] in cold (3).

$\bar{C}$ with [illegible] ether gives RMgCl; this upon oxidn with O_2 and subsequent hydrolysis yields (2) 2,2,3-trimethylbutanol-2, m.p. 80° (2).

$\bar{C}$ converted to RMgCl and the latter treated with CO_2 yields (2) *ter*-butyl-methylacetic acid [Beil II_2-(150)], m p 80° (2)

3:4020 (1) Butlerow, *Ann* **177**, 183–184 (1875). (2) Richard, *Ann. chim.* (8) **21**, 356–358 (1910). (3) Henry, *Compt. rend* **142**, 1024 (1906); *Rec trav chim.* **26**, 104 (1907). (4) Bartlett, Condon, Schneider, *J. Am Chem. Soc.* **66**, 1533, 1537 (1944).

3:4030 2,4,6-TRICHLOROPHLOROGLUCINOL



$C_6H_3O_3Cl_3$ Beil. VI - 1104
VI_1—
VI_2—

M.P. 136° u.c. (1)
134° (2)
132–133° (3)

Cryst. from abs. alc. — Note that from aq. C̄ cryst. as a trihydrate (1), but on htg. this hydrate loses aq. before melting (2); note also that C̄ on recrystn from toluene gives a solvated prod., m.p. 108–109° (1). [For study of crystallography of C̄ see (4).]

C̄ is alm. insol. aq. or cold C_6H_6; sol. alc. — C̄ readily sublimes.

[For prepn. of C̄ from phloroglucinol (1,3,5-trihydroxybenzene) (1:1620) with Cl_2 in CCl_4 (crude yield 76% (1)) or in AcOH (5) see indic. refs.; note that attempts (6) (7) to prepare C̄ from phloroglucinol (1:1620) with Cl_2 in aq. soln. were not effective owing to further decompn. of the prod. into dichloroacetic acid (3:6208) and/or the tetrahydrate of *sym.*-tetrachloroacetone (3:6050) cf. (1).]

[For formn. of C̄ from phloroglucinol (1:1620) with SO_2Cl_2 in dry ether see (3).]

[For formn. of C̄ from hexachlorocyclohexanetrione-1,3,5 ("hexachlorophloroglucinol") [Beil. VII-854, VII_1-(469)] by reduction with $SnCl_2$ or KI see (7).]

C̄ dis. in hot conc. HCl from which on cooling it separates in fine ndls.; C̄ with warm dil. HNO_3 is decomposed with formn. of oxalic acid (1:0445); C̄ with conc. H_2SO_4 dissolves unchanged on gentle warming, but on contd. htg. HCl is evolved and soln. turns deep sage-green (1).

C̄ dissolves in aq. alk. but is repptd. unchanged upon acidification; note, however, that alk. soln. of C̄ on stdg. in air develops a purple color (1).

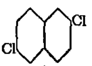
[C̄ in AcOH added to excess Br_2/aq. undergoes ring cleavage with formn. of 1,1,3,5,5-pentabromo-1,3,5-trichloropentanedione-1,4 [Beil. I-786], colorless cryst. from pet. ether, m.p. 93–95°, to a turbid liq. becoming clear at 98° (8).]

—— **2,4,6-Trichlorophloroglucinol trimethyl ether:** ndls. from alc., m.p. 130–131° (9). [Prepd. indirectly (9)]

—— **2,4,6-Trichlorophloroglucinol triacetate:** lfts. from dil. AcOH, m.p. 167–168° (7). [From C̄ with large excess AcCl at 100° (7).]

3:4030 (1) Webster, *J. Chem. Soc.* **47**, 423–426 (1885). (2) Zincke, Kegel, *Ber.* **23**, 1731–1732 (1890). (3) Peratoner, Finocchiaro, *Gazz. chim. ital.* **24**, I 243–244 (1894). (4) Déverin, *Bull*
C.A. **34**, 4320 (1940). (5) Hazura,
ɔermann, *Ann.* **155**, 132–134 (1870).
, Kegel, *Ber.* **23**, 1720–1721 (1890).
(9) Ciamician, Silber, *Ber.* **24**, 2980–2981 (1891).

3:4040 2,6-DICHLORONAPHTHALENE



$C_{10}H_6Cl_2$ Beil. V - *544*
V_1—
V_2-(446)

M.P. 136° (1) (2)
135–136° (13)
135–135.5° u.c. (3)
135° u.c. (4)
135° (5) (6) (7) (9) (19)

B.P. 285° u.c. (4)

Tbls. from ether + C_6H_6, ndls from hot alc., pr. from AcOH. — Spar. sol. alc.; eas. sol. ether, C_6H_6, or $CHCl_3$. — Volatile with steam.

[For prepn. of C̄ from naphthalene-2,6-*bis*-(sulfonyl chloride) [Beil. XI-216] (8) (10), from 6-chloronaphthalene-2-sulfonyl chloride [Beil. XI-180] (45% yield (2)) (1) (9), from 6-bromonaphthalene-2-sulfonyl chloride [Beil. XI-184] (11), from salts of 2-hydroxynaphthalenesulfonate-6 [Beil. XI-282, XI_1-(66)] (59% yield (3)) (4) (5), or from 6-bromonaphthol-2 [Beil. VI-651] (55% yield (12)) with PCl_5 as directed, see indic. refs.; from 6-sulfonaphthylamine-2 [Beil XIV-760, XIV_1-(735)] by treatment of corresp. diazonium chloride with PCl_5 in $POCl_3$ see (13) (14), from 2,6-diaminonaphthalene [Beil. XIII-208] via tetrazotization in HCl followed by htg. with Cu pdr. see (6), from sodium β-naphthalenesulfonate [Beil XI-171, XI_1-(38)] with $KClO_3$ + boilg dil HCl (50% yield) see (15).]

[C̄ in $CHCl_3$ satd. with Cl_2 gives (9% yield (20)) 1,2,6-trichloronaphthalene (3:2515), m.p. 92°.]

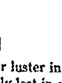
C̄ on oxidn. with dil. HNO_3 ($D = 1.2$) in s.t. at 150° (16) or better with dil. HNO_3 ($D = 1.13$) in s t. at 190–200° (17) yields 4-chlorophthalic acid (3:4390), m.p. 148° u c: (17). — C̄ on oxidn. with CrO_3/AcOH yields (18) 2,6-dichloronaphthoquinone-1,4 [Beil. VII-730], bright yel. ndls, m.p 148–149° (18), this cpd. also accompanies (18) the 4-chlorophthalic acid of the same m.p. during HNO_3 oxidn (above)

[C̄ on mononitration yields (16) two isomers, one m.p. 139–139.5°, the other m.p. 113.5–114° (16)]

[C̄ in CS_2 treated with $ClSO_3H$ yields (19) 2,6-dichloronaphthalenesulfonic acid-4 [Beil. XI-162] (corresp sulfonyl chloride, m.p. 136°, corresp. sulfonamide, m.p. 269°).]

3:4040 (1) Forsling, *Ber* **20**, 80–81 (1887). (2) Beattie, Whitmore, *J. Am. Chem Soc.* **55**, [illegible] B-20, 146–147 (1933). (4) Claus, [illegible]
Arnell, *Bull soc. chim* (2) **45**, 184 (1886) (10) Armstr [illegible]
(11) Sindall, *Chem. News* **60**, 58 (1889). (12) Franzen, Stauble, *J. prakt. Chem* (2) **103**, 370 (1921/22) (13) Erdmann, *Ann* **275**, 280 (1893). (14) Nakata, *Ber.* **64**, 2067 (1931). (15) Kozlov, Talybov, *J Gen. Chem. (U S S.R.)* **9**, 1827–1833 (1939), *C.A* **34**, 4067 (1940). (16) Alén, *Bull. soc. chim.* (2) **36**, 434 (1881). (17) Claus, *Ber.* **51**, 320 (1882). (18) Claus, Müller, *Ber.* **18**, 3073–3074 (1885) (19) Armstrong, Wynne, *Chem. News* **61**, 273–275 (1890). (20) Wynne, *J. Chem. Soc.* **1946**, 61.

3:4052 2,3,5-TRICHLOROHYDROQUINONE



$C_6H_3O_2Cl_3$ Beil. VI - 850
VI_1—
VI_2-(846)

M.P.
M.P. 138°	(1)
136°	(2)
134°	(3)
131–132°	(16)
130–132°	(13)
130°	(4)

[*See also* 2,3,5-*trichlorobenzoquinone*-1,4 (3:4672).]

Colorless shining pr. from aq. rapidly losing their luster in air (3); transparent pr. with 1 mole AcOH from AcOH but solvated AcOH readily lost in air (5).

C̄ at 15° is sol. in 160 pts. aq. (6); C̄ is spar. sol. cold aq. but eas. sol. hot aq. in which it first melts to an oil (3); C̄ is eas. sol alc. or ether.

C̄ readily sublimes in lfts. (4); for study of sublimation press. see (7).

[For study of heat of formn. of C̄ see (8); for studies of heat of combustion of C̄ see (5) (9).]

[For detn. of chlorine in C̄ by hydrogenation at elevated temp. see (10); for patent on use of C̄ as vulcanization accelerator see (11).]

PREPARATION OF C̄

From trichlorobenzoquinone. [For prepn. of C̄ from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) by reduction with aq. SO_2 (3) (4) (6) (12) in ether (1), or from " benzoquinone tetrachloride " (2,3,5,6-tetrachlorocyclohexanedione-1,4) [Beil. VII-557] with aq. SO_2 (13), see indic. refs.]

From other sources. [For formn. of C̄ (together with other products) from 2,5-dichlorobenzoquinone-1,4 (3:4470) or from 2,6-dichlorobenzoquinone-1,4 (3:3750) with boilg. conc. HCl see (14); from C_6H_6 with $KClO_3 + H_2SO_4$ see (16).]

CHEMICAL BEHAVIOR OF C̄

Reduction. [C̄ with Na/Hg in acid soln. is hardly affected and does *not* (3) give hydroquinone; however, for anal. of C̄ by quant. detn. of chlorine with H_2 at elev. temp. see (10).]

Oxidation. C̄ on oxidn., e.g., with CrO_3 at 0° (5), conc. HNO_3 (4) (3), $AgNO_3$ (4), or $FeCl_3$ (4), gives 2,3,5-trichlorobenzoquinone-1,4 (3:4672); note, however, that with insufficient oxidizing agent the corresp. quinhydrone (see below) may separate.

[For study of oxidn.-reductn. potential of system C̄ + 2,3,5-trichlorobenzoquinone-1,4 (3:4672) see (2) (17) (18).]

C̄ (1 mole) with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) (1 mole) in $CHCl_3$ soln. gives on evapn. (2) (19) the corresp. quinhydrone, green-black cryst., m.p. 114–115° (2), 103° (19).

[Note also that C̄ in aq. KOH exposed to air first turns green, then red, and finally brown (4), and this soln. on stdg. or boilg. in air gradually separates the corresp. potassium salt of chloranilic acid (3:4970) (3).]

Other reactions of C̄. [C̄ with PCl_5 (2 moles) on htg. gives (3) a mixture of pentachlorobenzene (3:2290) and hexachlorobenzene (3:4939).]

—— **Trichlorohydroquinone dimethyl ether** (3,4,5-trichloro-1,4-dimethoxybenzene): unreported.

Ⓓ **Trichlorohydroquinone diethyl ether** (3,4,5-trichloro-1,4-diethoxybenzene): ndls. from alc., m.p. 68.5° (3). [From C̄ with C_2H_5I + KOH in s.t. (3).]

Ⓓ **Trichlorohydroquinone diacetate**: ndls. by sublimation, m.p. 153° (3). [From C̄ with AcCl under reflux (3).]

Ⓓ **Trichlorohydroquinone dibenzoate**: ndls. from CS_2, m.p. 174° (14). [From C̄ with BzCl on htg. (14).]

3:4052 (1) Biltz, Giese, *Ber.* **37**, 4017 (1904). (2) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2206–2207 (1923). (3) Graebe, *Ann.* **146**, 22–30 (1868). (4) Städeler, *Ann.* **69**, 321–326 (1849). (5) Valeur, *Ann. chim.* (7) **21**, 496–499 (1900). (6) Stenhouse, *Ann. Suppl.* **6**, 218 (1868). (7) A. S. Coolidge, M. S. Coolidge, *J. Am. Chem. Soc.* **49**, 100–104 (1927). (8) Sjöstrom, *Svensk Kem. Tid.* **48**, 121–124 (1936); *Cent.* **1937**, I 58; *C.A.* **30**, 6634 (1936). (9) Swietoslawski, Starczewska, *J. chim. phys.* **22**, 399–401 (1925). (10) ter Meulen, Heslinga, *Rec. trav. chim.* **42**, 1093–1096 (1923).

(11) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, I 3134; *C.A.* **27**, 2845 (1933). (12) Graebe, *Ann.* **263**, 28 (1891). (13) Peratoner, Genco, *Gazz. chim. ital.* **24**, II 389–390 (1894). (14) Levy, Schultz, *Ann.* **210**, 153–154 (1881). (15) Krafft, *Ber.*

10, 797–800 (1877). (16) Carius, *Ann.* **142**, 129–138 (1867). (17) Conant, *J. Am Chem. Soc.* **49**, 293–297 (1927). (18) Kvalnes, *J. Am. Chem. Soc.* **56**, 667–670 (1934). (19) Ling, Baker, *J. Chem. Soc.* **63**, 1322–1323 (1893).

3:4065 3-CHLORO-4-HYDROXYBENZALDEHYDE  $C_7H_5O_2Cl$ Beil. VIII - 81 $VIII_1$—

M.P. 139° cor. (1) **B.P. 149–150° at 14 mm. (1)**
132–134° (2)
127–128° (3)

Ndls. from aq. (1). — *Very spar. sol. cold aq., eas. sol. hot aq.*; spar. sol. $CHCl_3$; eas. sol. alc., ether (1).

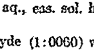
[For prepn. of C̄ from *p*-hydroxybenzaldehyde (1:0060) with Cl_2 + $CHCl_3$ see (1) (2); from 3-chloro-4-hydroxybenzyl alcohol by htg. with alk. sodium *m*-nitrobenzenesulfonate see (3); from *o*-chlorophenol (3:0255) + CH_2O under specified circumstances see (4) or with chloral (3:5210) see (5).]

C̄ with $FeCl_3$ gives no coloration (3). — C̄ forms a $NaHSO_3$ cpd. (3).

C̄ in EtOAc hydrogenated with H_2 at 40 lb./sq. in. for 45 min. in presence of Raney Ni cat. gives (2) 3-chloro-4-hydroxybenzyl alc., cryst. from C_6H_6, m.p. 127° (2).

Ⓓ **3-Chloro-4-hydroxybenzaldoxime:** ndls. from aq. or $CHCl_3$, m.p. 144–145° (1).
—— **3-Chloro-4-hydroxybenzaldehyde phenylhydrazone:** unrecorded.
—— **3-Chloro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** unrecorded.
—— **3-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.
Ⓓ **3-Chloro-4-hydroxybenzaldehyde semicarbazone:** yel. ndls from very dil. AcOH, m p. 210° dec. (1); 212° (3).

3:4065 (1) Biltz, *Ber.* **37**, 4031–4034 (1904). (2) Buehler, Brown, Holbert, Fulmer, Parker, *J. Org Chem.* **6**, 904 (1941). (3) Hanus, *J prakt. Chem.* **158**, 263 (1941). (4) Geigy and Co., Ger 105,798; *Cent.* **1900**, I 523. (5) Haakh, Smola, Austrian 151,159, March 25, 1935; *Cent.* **1935**, I 439.

3:4085 2-CHLORO-3-HYDROXYBENZALDEHYDE  $C_7H_5O_2Cl$ Beil. S.N. 745

M.P. 139.5° (1)
139–139.5° (3)
139° cor. (4)

Colorless cryst from dil. AcOH (1) becoming pale pink on prolonged exposure to air (1) — C̄ has pronounced sternutatory props. (1) (3).

[For prepn of C̄ from *m*-hydroxybenzaldehyde (1:0055) + Cl_2 (32 6% yield (4)) see (1) (3) (4); for indirect prepn. via 2-nitro-3-hydroxybenzaldehyde, reductn., and appropriate diazo reactns. see (1).]

C̄ in 50% AcOH mononitrated as directed (2) by grad. addn. of HNO_3 (D = 1.3) then after a min. poured onto ice gives 100% yield of mixt. of 4-nitro and 6-nitro derivs.; extraction with aq. at 00° dissolves the latter leaving residue of almost pure 4-nitro deriv.; from the soln. of 6-nitro isomer a little dissolved 4-nitro cpd. is distilled out with steam (2).

4-Nitro-2-chloro-3-hydroxybenzaldehyde: pale yel. ndls. from AcOH, m p 166° (2). [Corresp. oxime, insol. aq., yel. ndls. from alc., m p. 170° (2); *p*-nitrophenylhydrazone, deep or. ndls from hot AcOH, m p. 294–295° dec. (2); semicarbazone, sulfur-yel. ndls.

from hot alc., m.p. 271–272° dec. (2); methyl ether, colorless ndls. from dil. alc. or dil. AcOH, m.p. 107° (2).]

6-Nitro-2-chloro-3-hydroxybenzaldehyde: colorless ndls. from aq., m.p. 153° (2). [Corresp. oxime, exceedingly sol. in aq. or alc., colorless ndls. from $CHCl_3$, m.p. 175° (2); *p*-nitrophenylhydrazone, or.-red ndls. from hot dil. AcOH, m.p. 232–233° (2); semicarbazone, pale yel. ndls. from alc., m.p. 234° dec. (2); methyl ether, colorless ndls. from AcOH, *m.p. 134° (2).]*

C̄ in $CHCl_3$ treated with Br_2 in $CHCl_3$ as directed (5) gives (86% yield (5)) 4-bromo-2-chloro-3-hydroxybenzaldehyde, cryst. from 50% AcOH, m.p. 139–140° cor. (5). [This deriv. depresses m.p. of C̄ (5).] [4,6-Dibromo-2-chloro-3-hydroxybenzaldehyde has m.p. 104–105° (5).]

C̄ with 50% KOH at 60–70° undergoes Cannizzaro reactn. giving (4) 2-chloro-3-hydroxybenzyl alc. (87% theory (4)), cryst. from toluene, m.p. 132° cor. (4), and 2-chloro-3-hydroxybenzoic acid (90% theory (4)) (3:4395), cryst. from aq., m.p. 156° (4).

C̄ in aq. 20% NaOH (1) or aq. $NaHCO_3$ (1), treated with Me_2SO_4, yields methyl ether (2-chloro-3-methoxybenzaldehyde), volatile with steam, cryst. from dil. alc., m.p. 56–57° (1). [This ether depresses m.p. of corresp. deriv. (m.p. 52°) of the isomeric 4-chloro-3-hydroxybenzaldehyde (3:3780).] *[On oxidn. with alk. $KMnO_4$ (1) this methyl ether yields* 2-chloro-3-methoxybenzoic ac., m.p. 160° (1).]

Ⓓ **2-Chloro-3-hydroxybenzaldoxime:** colorless ndls. from dil. alc., m.p. 149° (1).

—— ***2-Chloro-3-hydroxybenz ldehyde phenylhydrazone:*** *unrecorded.*

Ⓓ **2-Chloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** or.-red ndls. from hot alc., m.p. 244–245° (1).

—— **2-Chloro-3-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.

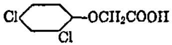
Ⓓ **2-Chloro-3-hydroxybenzaldehyde semicarbazone:** pale yel. ndls., m.p. 236–237° (1).

Ⓓ **2-Chloro-3-acetoxybenzaldehyde:** rhombic cryst. from alc., m.p. 62° (1).

Ⓓ **2-Chloro-3-benzoxybenzaldehyde:** rhombic cryst. from alc., m.p. 88° (1).

3:4085 (1) Hodgson, Beard, *J. Chem. Soc.* **1926**, 149–155. (2) Hodgson, Beard, *J. Chem. Soc.* **1926**, 2031–2036. (3) Bissell, Kranz (to National Aniline and Chem. Co.), U.S. 1,776,803, Sept. 30, 1930; *Cent.* **1931**, II 159; *C.A.* **24**, 5768–5769 (1930). (4) Lock, *Monatsh.* **55**, 309–311 (1930). (5) Lock, *Monatsh.* **62**, 187–188 (1933).

3:4095 2,4-DICHLOROPHENOXYACETIC ACID $C_8H_6O_3Cl_2$ Beil. S.N. 522



M.P. 140–141° (1)
138° (2)

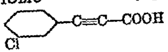
White odorless cryst. from C_6H_6; alm. insol. aq. — Neut. Eq. = 221.0.

[For prepn. of C̄ from 2,4-dichlorophenol (3:0560) with chloroacetic acid (3:1370) in aq. NaOH (87% yield) see (1).]

[For general survey of C̄ as plant hormone see *(1) (3) cf. (4); for use of* solns. of C̄ in polyethylene glycols for regulating growth of plants see (5); for use of C̄ as weed killer see (6).]

3:4095 (1) ... –991 (1943). (2) Pokorny, *J. Am. Chem. Soc.* **63**, 1768 (... *Contrib. Boyce Thompson Inst.* **12**, 321–343 (1942); *C.A* ... r, Shalvia, *Botan. Gaz.* **104**, 281–287 (1942); *C.A.* **37**, 1 ... *Botan. Gaz.* **105**, 474–483 (1944); *C.A.* **38**, 4654 (1944). (6, ... (1944).

:4102 *m*-CHLOROPHENYLPROPIOLIC ACID $C_9H_5O_2Cl$ Beil. S.N. 950



M.P. 140–141° (1)

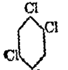
Cryst. from AcOH.

[For prepn. of Č from *m*-chlorobenzaldehyde (3:6475) by conversion through *m*-chlorocinnamic acid to ethyl *m*-chlorocinnamate, thence by addn. of Br_2 to give ethyl β-(*m*-chlorophenyl)-α,β-dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see (1).]

Č with $Cu(OAc)_2$ loses CO_2 yielding (1) *m*-chlorophenylacetylene (3:9500) (cf. also under *o*-chlorophenylpropiolic acid (3:3956)).

3:4102 (1) Otto, *J. Am. Chem. Soc* 56, 1393–1394 (1934).

3:4115 1,2,4,5-TETRACHLOROBENZENE $C_6H_2Cl_4$ Beil. V - 205
V₁-(113)
V₂-(157)



M.P.	141°	(1)	B.P. 243–246° cor.	(9)
	140–141°	(2)	240°	(5)
	139.6–139.9°	(3)	236°	(7)
	139.5–140.5°	(4)		
	139°	(5) (6) (24)		
	138°	(7) (8) (13) (14)		
	137–138°	(9) (10)		
	137.5°	(11)		
	137°	(12) (23)		

Ndls. from ether; cryst. from CCl_4, CS_2, C_6H_6 + EtOH, or C_6H_6 (for studies on crystallographic props. see (2) (8) (5) (15)). — Insol. cold and spar. sol. hot alc; fairly sol cold ether, C_6H_6, $CHCl_3$, or CS_2 — Č has penetrating and disagreeable odor. — Sublimes easily.

[For prepn of Č from 2,4,5-trichloroaniline [Beil. XII-627] (9) or from 2,5-dichloro-*p*-phenylenediamine [Beil XIII-118] (16) via diazotization and use of Cu_2Cl_2 reactn. (64% yield (16)) see indic refs; from *p*-dichlorobenzene (3:0980) with S_2Cl_2 + $AlCl_3$ in SO_2Cl_2 (67% yield (1)) (17) or from *o*-dichlorobenzene (3:6055) with Cl_2 + cat. (18) see indic. refs]

[For formn of Č from C_6H_6 with Cl_2 in pres. of I_2 (5), Fe (44% yield (13)), or $AlCl_3$ (19), or Cu (20), or from chlorobenzene with Cl_2 + Cu (20), or from *o*-dichlorobenzene (3:6055) with Cl_2 + cat (18) or Al/Hg (21), or from *m*-dichlorobenzene (3:5960) with Cl_2 + Al/Hg (21) or $AlCl_3$ (4), or from *p*-dichlorobenzene with Cl_2 in pres. of Fe (39% yield (13)), see indic refs, from dry C_6H_6 with anhyd. $AuCl_3$ (22) or on electrol in aq. HCl/AcOH soln see (23); from lower chloro derivs. of C_6H_6 with $FeCl_3$ see (7); from 2,4,5-trichlorotoluene (3.2100) with Cl_2 see (24); from benzaldehyde (1:0195) by htg. with $SbCl_5$ see (11)]

[For formn of Č from 2,5-dichloro-4-nitroaniline on diazotization and treatment with Cu_2Cl_2 see (25) (14) (note abnormal replacement of nitro group); from nitrobenzene with SO_2Cl_2 + N_2O_4 see (10), from resorcinol 4,6-*bis*-(sulfonyl chloride) or hydroquinone 2,5-

bis-(sulfonyl chloride) with PCl_5 in s.t. at 180° see (12) (26); from 4,6-dichlorobenzene 1,3-*bis*-(sulfonyl chloride) (27) or from 1,3-*bis*-(methylmercapto)benzene-4,6-*bis*-(sulfonyl chloride) (28) with $SOCl_2$ at 170–200° see indic. refs.; from 2,5-dichlorobenzene-1,4-*bis*-(sulfonyl chloride) with PCl_5 in s.t. 4 hrs. at 180° see (6); from 2,3,5,6-tetrachloro-*N*-nitroacetanilide (39) by refluxing in toluene or xylene (other products are also formed) see (39).]

[For behavior of C̄ with liq. Cl_2 yielding addn. products see (29); for behavior with NH_3 at elevated temps. see (30); C̄ with S_2Cl_2 + $AlCl_3$ + SO_2Cl_2 yields (17) hexachlorobenzene (3:4930).]

[C̄ htd. with NaOMe as directed yields according to conditions (13) (31) (32) (38) 2,4,5-trichlorophenol (3:1620) or its methyl ether.]

C̄ on mononitration, e.g., on boilg. with 5 pts. HNO_3 (D = 1.52) for ½ hr. (3) (13) (34), yields 1,2,4,5-tetrachloro-3-nitrobenzene [Beil. V-247], m.p. 99–100° (33) (35), 99° (34) (13), 98° (9), some tetrachlorobenzoquinone (chloranil) (3:4978) (insol. in pet. ether) also being formed (9) (34) (13) (33). [For studies on chem. of this mononitro cpd. see (36).]

C̄ on dinitration by boilg. 5–6 hrs. with mixt. of 10 pts. HNO_3 (D = 1.52) + 10 pts. fumg. H_2SO_4 (25% SO_3) gives (71% yield (33)) 1,2,4,5-tetrachloro-3,6-dinitrobenzene, cryst. from C_6H_6 by addn. of alc., m.p. 227–228° (33), 232–233° (35).

C̄ with 4 pts. chlorosulfonic acid refluxed for hr. gives (78% yield (37)) hexachlorobenzene (3:4930), m.p. 218–219° u.c. (37).

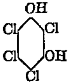
3:4115 (1) Silberrad, *J. Chem. Soc.* **121**, 1020 (1922). (2) Fels, *Z. Krist.* **32**, 365 (1900). (3) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 434 (1932). (4) Olivier, *Rec. trav. chim.* **39**, 411–413 (1920). (5) Jungfleisch, *Ann. chim.* (4) **15**, 277–283 (1868). (6) Gebauer-Fulnegg, Fidor, *Monatsh.* **48**, 634 (1927). (7) Thomas, *Compt. rend.* **126**, 1212 (1898). (8) Bodewig, *Z. Krist* **3**, 400 (1879). (9) Beilstein, Kurbatow, *Ann.* **192**, 236–237 (1878). (10) Battegay, Denivelle, *Bull. soc. chim.* (4) **47**, 609 (1930).

(11) Gnehm, Banziger, *Ann.* **296**, 67 (1897). (12) Litvay, Riesz, Landau, *Ber.* **62**, 1867 (1929). (13) Holleman, *Rec. trav. chim.* **39**, 736–737, 745, 749 (1920). (14) Hodgson, *J. Soc. Dyers Colourists* **42**, 368 (1926). (15) Groth, *Chem. Krist.* **4**, 7 (1917). (16) Schoutissen, *J.*

...3,200, March 7, 1933; *Cent.* 1028 (1898). ...28, I 2370. *J. Am. Chem.* ...4) Beilstein, **40**, 71 (1921). *Monatsh.* **35**, ...

... (1925). (34) ...*boensis Math.* ...we, Stead, *J.* ... (1940). (38) ... **943**, 372–373.

3:4135 TETRACHLORORESORCINOL



$C_6H_2O_2Cl_4$ Beil. VI - 820
VI_1—
VI_2-(819)

M.P. 141° (1)
140° (2)

Long colorless ndls. from hot aq. — Faintly pleasant phenolic odor. [New comml. rod (1942) in U.S.A.] — Eas. sol. alc., ether, AcOH, C_6H_6; fairly eas. sol. hot aq.; spar. ol. cold aq.

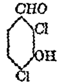
[For prepn. from "hexachlororesorcinol" (3:3470) by reduction with $SnCl_2$ in AcOH ee (1).]

C̄ is sol. in aq. alk. (2). — C̄ in aq. soln. gives with $FeCl_3$ a blue color (2).

C̄ in AcOH on treatment with Cl_2 yields "hexachlororesorcinol" (3:3470), m.p. 115°.

Ⓓ Tetrachlororesorcinol diacetate: m.p. 145° (1), 144° (2). [Note that m.p. of this deriv. is close to that of C̄ and should be tested by method of mixed m.p.'s.]

:4135 (1) Zincke, Fuchs, *Ber.* **25**, 2689–2690 (1892). (2) Fries, Hartmann, *Ber.* **54**, 199 (1921).

3:4140 2,4-DICHLORO-3-HYDROXYBENZ-ALDEHYDE  $C_7H_4O_2Cl_2$ Beil. S.N. 745

M.P. 141° (1)

Colorless cryst. from AcOH. C̄ has pronounced sternutatory props. and blisters moist skin. — [Note that the m.p. of a mixt. of C̄ with isomeric 2,6-dichloro-3-hydroxybenzaldehyde (3:4160), m.p. 140°, is depressed to 111° (1).]

[For prepn. of C̄ from 4-chloro-3-hydroxybenzaldehyde (3:3780) in AcOH with Cl_2 at room temp. (100% yield) see (1).]

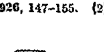
C̄ (1 pt.) in AcOH (4 pts.) on nitration at 65° with 1 pt. conc. HNO_3 (D = 1.42) yields (2) 2,4-dichloro-3-hydroxy-6-nitrobenzaldehyde (2), colorless ndls. from its deep yellow soln. in AcOH or from hot aq., m.p. 107° (2) (p-nitrophenylhydrazone, or. ndls. from AcOH, m.p. 279–280° (2), semicarbazone monohydrate, yel. ndls. from dil. alc., softens 140–150° (2))

C̄ dislvd. in boilg. 10% NaOH (2 moles) and treated with Me_2SO_4 (1.3 moles) yields (1) 2,4-dichloro-3-methoxybenzaldehyde, m.p. 82° (1) (p-nitrophenylhydrazone, old-gold ndls., m.p. 258–260° (1)), which on oxidn. yields 2,4-dichloro-3-methoxybenzoic acid, colorless ndls., m.p. 163° (1).

Ⓓ 2,4-Dichloro-3-hydroxybenzaldoxime: fine colorless ndls. from alc., m.p. 188° (1).

Ⓓ 2,4-Dichloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone: or.-red ndls., m.p. 277–278° dec. (1)

3:4140 (1) Hodgson, Beard, *J. Chem. Soc.* **1926**, 147–155. (2) Hodgson, Beard, *J. Chem. Soc.* **1926**, 2030–2036.

3:4150 *o*-CHLOROBENZOIC ACID  $C_7H_5O_2Cl$ Beil. IX - 334, IX_1-(138)

M.P.	**142°**	(1) (2) (3)	**139.9°**	(15)
	141.8°	(4)	**139.8–140.0°**	(16)
	141°	(5) (6) (7) (8) (181)	**139.5–140°**	(17)
	140–142°	(9)	**139.5°**	(38)
	140.65°	(10)	**139–140°**	(18) (19)
	140.3°	(11) (29)	**139°**	(20) (21) (22)
	140.2°	(12)	**138°**	(23) (24) (58)
	140°	(13) (14) (26) (27) (49)	**137°**	(25) (63) (97) (36)

Cryst. from hot aq., C_6H_6, dioxane/C_6H_6, or alc. — $\bar{C}$ is spar. sol. cold aq.; e g., $\bar{C}$ is sol. at 0° in 881 pts. aq. (27); at 25°, 100 ml. satd. aq. soln. conts. 0.213 g $\bar{C}$ (21) (= 0.0136 mole per liter (21) (28)) — $\bar{C}$ is eas. sol. hot aq., alc., ether (26). — At 14–16°C 100 ml. satd. soln. of $\bar{C}$ in acetone conts. 28.4 g. $\bar{C}$, in ether 17 g. $\bar{C}$, in EtOAc 13.2 g. $\bar{C}$, in 75% AcOH 6.2 g. $\bar{C}$; in C_6H_6 0.9 g. $\bar{C}$; in CCl_4 0.6 g. $\bar{C}$; in CS_2 0.5 g. $\bar{C}$; in lgr. 0.07 g. $\bar{C}$ (10). — For study of soly. of $\bar{C}$ in acetone (4), C_6H_6 (4) (29), heptane (29), chlorobenzene (3:7903) (30), o-chlorotoluene (3:8245) (30), or m-chlorotoluene (3:8275) (30) see indic. refs.

For study of distribution at 25° of $\bar{C}$ between aq. + toluene (31), aq. + xylene (32), or aq. + $CHCl_3$ (31) (32) (for use of $CHCl_3$ in sepn. of $\bar{C}$ from aq. suspension of 3-chlorophthalic acid (3:4820) (33)) see indic. refs.; for adsorption of $\bar{C}$ on charcoal from its solns. in EtOH (34), acetone (4), C_6H_6 (4), or aq. (35) see indic. refs.; for soly. of $\bar{C}$ in aq. solns. of various salts (including Na$\bar{A}$) see (28) (21).

$\bar{C}$ can be sublimed in vac. (12). — $\bar{C}$ is but very slightly volatile with steam (for details see (11)). — For crystallographic data see (36) (37). — For purification of $\bar{C}$ (by use of decolorizing carbon on soln. of $\bar{C}$ in aq. Na_2CO_3 followed by repptn. with 6 N HCl) see (38).

Binary systems contg. $\bar{C}$: for f.p./compn. data on system $\bar{C}$ + H_2O see (39); for f.p./compn. data and diagram on system $\bar{C}$ + BzOH (1:0715), eutectic, m.p. 91.1°, contg. about 41 wt. % $\bar{C}$, see (10) (41); for f.p./compn. data on systems $\bar{C}$ + o-toluic acid (1:0690) (20) or $\bar{C}$ + o-hydroxybenzoic acid (salicylic acid) (1:0780) (20) see indic. refs.

For f.p./compn. data and diagrams on systems $\bar{C}$ + m-chlorobenzoic acid (3:4392) (eutectic, m.p. 110.7°, contg. 52–53 mole % $\bar{C}$ (6) (40) (10) (15)) see indic. refs.; on system $\bar{C}$ + p-chlorobenzoic acid (3:4940) (eutectic, m.p. 132°, contg abt. 86 mole % $\bar{C}$) see (10) (15).

For f.p./compn. data and diagrams on systems $\bar{C}$ + o-bromobenzoic acid (41), $\bar{C}$ + o-iodobenzoic acid (42), $\bar{C}$ + o-nitrobenzoic acid (43), $\bar{C}$ + m-nitrobenzoic acid (43) see indic. refs.

Ternary systems contg. $\bar{C}$. [For influence of addn. of benzoic acid (6) or of p-chlorobenzoic acid (3:4940) (40) to the eutectic of $\bar{C}$ with m-chlorobenzoic acid (3:4392) see indic. refs.; for influence of addn. of $\bar{C}$ to the eutectic of benzoic acid with m-chlorobenzoic acid see (40); for data on system $\bar{C}$ + m-chlorobenzoic acid (3:4392) + p-chlorobenzoic acid (3:4940), eutectic, m.p. 104.9°, contg. respectively 48.3, 44.0, and 7.7 mole % of the three isomers, see (15).]

Miscellaneous. [For study of fate of $\bar{C}$ in animal organism see (44) (45); note that contrary to earlier (45) results with dogs and rabbits conjugation with glycine to yield the expected N-(o-chlorobenzoyl)glycine (o-chlorohippuric acid) [Beil. IX-336], m.p. 176° (45), does (44) occur. — For study of use of $\bar{C}$ (or its salts) as preservatives see (46); for detectn. of $\bar{C}$ in foods see (179). — For use of $\bar{C}$ as vulcanization regulator see (47) (48).]

Preparation. [For prepn. of $\bar{C}$ from o-chlorotoluene (3:8245) by oxidn. with boilg. aq. $KMnO_4$ (yields: 90% (14), 74–78% (18), 68–71% (24)) (49) (13), with nitrosulfonic acid (from fumg. HNO_3 + dry SO_2) at 100° (50), with air in the pres. of various catalysts (51) (52) (53), or in aq. alk. at 260° under press. (54), see indic. refs.; for formn. of $\bar{C}$ from o-chlorophenyl benzyl ketone by auto-oxidn. in light and air see (56); for formn. of $\bar{C}$ from o-chlorobenzaldehyde (3:6410) by oxidn. with CrO_3 (57), with alk. $KMnO_4$ (58), or by auto-oxidn. in Ac_2O (59) see indic. refs.]

[For prepn. of $\bar{C}$ from o-aminobenzoic acid (anthranilic acid) [Beil. XIV-312, XIV_1-(529)] via diazotization and use of Cu_2Cl_2 (yields: 90% (24), 87% (178)) (preferably under CO_2 (60)), or CuH (60% yield (61)), or Cu (62) see indic. refs.]

[For prepn. of $\bar{C}$ from o-chlorobenzonitrile [Beil. IX-336] by hydrolysis with H_2SO_4 (14), with dil. HCl in s t. at 150° (63), or boilg. KOH (14) see indic. refs.; from o-chlorobenzoyl chloride (3:6640) by hydrolysis with aq. (91) or aq. alk.; from o-chlorobenzotri-

chloride (3:6880) by hydrolysis (64) (65), e.g., with aq. in s.t. at 150° (27) or by boilg. conc. HNO_3 (65) see indic. refs.; from *o*-chlorobenzal (di)chloride (3:6625) with CrO_3 (57) or with boilg. aq. for 20 hrs. followed by oxidn. with $KMnO_4$ (75% yield (7)); from a mixt. of *o*-chlorobenzotrichloride + *o*-chlorobenzal (di)chloride by hydrol. with 70% H_2SO_4 or 80% AcOH or 5% NaOH at 90–100° in stream of air to effect immediate oxidn. (67); from *o*-chlorobenzoyl-*o*-chlorotriphenylmethane by hydrolytic cleavage with 20% MeOH/KOH 5 hrs. at b.p. (8); from *o*-chlorophenylnitrolic acid by hydrolysis with boilg. aq. (19) see indic. refs.]

[For formn. of $\bar{C}$ (together with other prods.) from benzoic acid (1:0715) with $KClO_3$ + HCl (68), with NaOCl (6) (69), see indic. refs.]

[For formn. of $\bar{C}$ from *o*-sulfobenzoic acid imide (saccharin) [Beil. XXVII-168, $XXVII_1$-(266)] with $KClO_3$ + HCl see (9); from 3-chlorophthalic acid (3:4820) by cat. monodecarboxylation see (70); from *o*-nitrotoluene [Beil. V-318, V_1-(158), V_2-(243)] (71), from sodium *o*-toluenesulfonate [Beil. XI-83, XI_1-(22)] (72), or from *o*-toluenesulfonyl chloride [Beil. XI-86, XI_1-(23)] (71) with $SOCl_2$ in s.t. at elevated temp. followed by treatment with aq. see indic. refs.]

Chemical behavior. [$\bar{C}$ (as $Na\bar{A}$) on reduction with Na/Hg (27) (25) (73) or $\bar{C}$ (as $K\bar{A}$) on fusion with sodium formate (74) cf. (75) is dehalogenated yielding benzoic acid (1:0715) (for study of reduction of $\bar{C}$ with H_2 + Ni in aq. alk. at ord. temp. see (76)). — $\bar{C}$ on electrolytic reduction in alc. H_2SO_4 yields (77) *o*-chlorobenzyl alc. [Beil. VI-444, VI_1-(222)], ndls. from aq. alc., m.p. 72° (77).]

$\bar{C}$ behaves normally as a monobasic acid: e.g., $\bar{C}$ on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization const. at 25° is 13.2×10^{-4} (78) (79) cf. (80) (81) (21) (1). — [For study of acid strength of $\bar{C}$ in various alcohols (82) (83) (84) (5) (85) (86) (22) or in acetonitrile (87) see indic. refs. — For solubility of $\bar{C}$ in aq. solns. of various salts incl. $Na\bar{A}$ see (28) (21). — For sepn. of $\bar{C}$ from *p*-chlorobenzoic acid (3:4940) by use of difference in their acidic strength see (88). — For use of $\bar{C}$ as standard in alkalimetry (89) and in iodimetry (90) see indic. refs.]

Salts of inorg. bases. [$NH_4\bar{A}$ (91) (92) (note that this salt with benzotrichloride (3:6880) in pres. of suitable cat. yields (93) *o*-chlorobenzonitrile). — Hydroxylamine salt: m.p. 104.5° (94). — $Na\bar{A}$ (use as preservative) (46). — $K\bar{A}.\frac{1}{2}H_2O$ (91) (forms liq. cryst. on fusion (95)). — $Ag\bar{A}$, scales from boilg. aq. (25) (100) (note that this salt with I_2 in C_6H_6 under reflux does *not* (96) yield phenyl *o*-chlorobenzoate, m.p. 37°, and thus differs from corresp. salt of *m*-chlorobenzoic acid (3:4392)). — $Ca\bar{A}_2.H_2O$ (26) (97), much more sol. aq. than corresp. salts of *m*-chlorobenzoic acid (3:4392) or *p*-chlorobenzoic acid (3:4940) (97); insol. either cold or hot alc. (98); on dry distn. gives (18% yield (99)) xanthone (1:7275), m.p. 174°. — $Ba\bar{A}_2.3H_2O$ from spont. evapn. of aq. soln. (98) (9). — $Ba\bar{A}_2$ from hot conc. aq. soln. (25) (26) (use in sepn. of $\bar{C}$ from isomers (40)); spar. sol. aq. (100). — Note that $Pb\bar{A}_2$ (25) (100) and $Cu\bar{A}_2$ (25) (100) are spar. sol. aq., while salts of Ca, Sr, Mg, Zn, Fe, Mn, Co, Ni, and Cd are sol. (100). — For sepn. of $\bar{C}$ from BzOH (1:0715) by use of Cu salts see (6).]

Salts of organic bases. $\bar{C}$ with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (101) benzylammonium *o*-chlorobenzoate, m.p. 148.4–149.4° u.c., 150.5–151.5° cor., Neut. Eq. 263.6 (note that the m.p. of this salt is but very slightly dif. from that of corresp. salt of *m*-chlorobenzoic acid (3:4392)). — $\bar{C}$ similarly treated with α-phenylethylamine yields (101) α-phenylethylammonium *o*-chlorobenzoate, m.p. 128.4–129.4° u.c., 130.9–131.9° cor., Neut. Eq. 277.6 (note that m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to those of the corresp. salts of *m*-methoxybenzoic acid, *p*-methoxybenzoic acid, and *o*-nitrobenzoic acid).

$\bar{C}$ (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd. several minutes, solvent evapd. and resulting sirup recrystd. from aq. yields (102) codeine *o*-chlorobenzoate, $C_{18}H_{21}O_3N.\bar{C}$, m.p. 134° on "Maquenne block"; note that this value although close to that of corresp. prod. from *o*-bromobenzoic acid is widely different from that of corresp. salts of either *m*-chlorobenzoic acid (3:4392) or *p*-chlorobenzoic acid (3:4940) which are 96° and 162° respectively. — $\bar{C}$ (1 mole) in alc. (or $CHCl_3$) with strychnine (1 mole) in alc, boiled for a few minutes, then cooled, yields (103) strychnine *o*-chlorobenzoate, $C_{21}H_{22}O_2N_2.\bar{C}$, m.p. 170° u.c. on "Maquenne block"; note that this melting point is somewhat lower than that (185°) for the corresp. salt of *m*-chlorobenzoic acid (3:4392) and widely different from that (251°) of the corresp. salt of *p*-chlorobenzoic acid (3:4940).

[For optical data on cinchonine salt see (104); for salt (m.p. 108–110°) with phenylmercuric hydroxide see (105).]

$\bar{C}$ with alcohols gives by conventional processes the corresp. esters; for details on methyl *o*-chlorobenzoate (3:6695) and ethyl *o*-chlorobenzoate (3:6800) see these compds. — [For study of rate of esterification of $\bar{C}$ with MeOH (106) (111) (17) (112), with EtOH (2) (17) (113), or with cyclohexanol (1:6415) (107) see indic. refs.]

$\bar{C}$ with P_2O_5 in toluene boiled for 4 hrs. (108), or $\bar{C}$ (109) or its sodium salt (110) refluxed with oxalyl (di)chloride (3:5060) in C_6H_6, yields *o*-chlorobenzoic acid anhydride, ndls. from lt. pet. (108) or alc. (109), m.p. 79.6° (108), 78–79° (109); note that $\bar{C}$ (2 moles) with oxalyl (di)bromide refluxed in C_6H_6 similarly gives good yields (110) of the above anhydride, but that $Na\bar{A}$ with oxalyl (di)bromide can also be used (110) to give *o*-chlorobenzoyl bromide, b.p. 143–145° at 37 mm. (110).

$\bar{C}$ with PCl_5 (114) (45) (115), or with $PCl_3 + ZnCl_2$ (114), or with $SOCl_2$ (114) (45) (116) (117), or with $SOCl_2$ + pyridine (118), or with *o*-chlorobenzotrichloride (3:6880) + $ZnCl_2$ (119) yields *o*-chlorobenzoyl chloride (3:6640) q.v. for data on yields.

$\bar{C}$ with KOH or NaOH on fusion (128) (27) (25), or $\bar{C}$ with aq. piperidine in pres. of Cu powder in s.t. at 160° for 4 hrs. (121), or $\bar{C}$ with aq. piperidine + Na_2CO_3 + amyl alc. + Cu powder refluxed 6 hrs. (124), or $\bar{C}$ (as $K\bar{A}$) with aq. NaOAc + $Cu(OAc)_2$ in s t. at 140–150° for 9–10 hrs. (126), or $\bar{C}$ with aq. $Ca(OH)_2$ + Cu cpds. at 160–170° under press. (122) gives (83% yield (126)) *o*-hydroxybenzoic acid (salicylic acid) (1:0780), accompanied in some cases (120) by substantial amounts of *m*-hydroxybenzoic acid (1:0825). — For use of alk. fusion as means of detect. of $\bar{C}$ in wine see (123). — Note that $\bar{C}$ with aq. KOH (even in pres. of copper) (124), or $\bar{C}$ with aq. $Ba(OH)_2$ in s.t. at 190–200° (125), does not yield salicylic acid or any chloride ion.

Reaction of $\bar{C}$ with phenols. $\bar{C}$ on suitable treatment condenses with phenols yielding *o*-aryloxybenzoic acids: e g, $\bar{C}$ (as $K\bar{A}$) with Na phenolate and Cu powder at 180–190° for 5 min. (127) (128), or $\bar{C}$ (as $K\bar{A}$) with phenol + Cu powder or Cu salts (129) (130), or $\bar{C}$ (as $K\bar{A}$) with anhydrous KOAc/NaOAc + Cu powder at 245–255° for 5 hrs. (126) gives (90% yield (127)) *o*-phenoxybenzoic acid [Beil. X-65, X_1-(28)], lfts. from dil. alc., m.p. 113°; note that this prod. with conc. H_2SO_4 on gentle warming loses H_2O and ring-closes in quant. yield (131) to xanthone (1:7275), m.p. 174°. — [For analogous condensations of $\bar{C}$ with *o*-cresol (1:1400) (127) (128) (60), *m*-cresol (1:1730) (127), *p*-cresol (1:1410) (127) (128), α-naphthol (1:1500) (132), β-naphthol (1:1540) (127) (128), *o*-chlorophenol (3:5980) (133), *m*-chlorophenol (3:0255) (133), *p*-chlorophenol (3:0495) (133), *m*-nitrophenol (133), *p*-nitrophenol (133), including conv. to the corresp. xanthones, see indic. refs.; many other analogous cases are known but cannot be included here.

Reaction of $\bar{C}$ with amines. $\bar{C}$ (or its salts) with primary or secondary aliphatic or aromatic amines in the pres. of K_2CO_3 and Cu powder on htg. condenses with elimination of HCl (or its equivalent) to yield products of type *o*-HOOC—C_6H_4—NHR; these products by ring closure through elimination of water yield in turn the corresponding acridones; the

reaction has been executed for countless cases of which only a few of the more important examples can be cited here; for the most comprehensive single survey see (134).

$\bar{C}$ (as K$\bar{A}$) htd. with aq. aniline + Cu powder (134) (135), Cu salts (135), or $\bar{C}$ htd. with aniline + Cu powder (136) or Cr powder (137), or $\bar{C}$ htd. with aniline + anhydrous K_2CO_3 + CuO (134) (38) gives (yields: 97% (134), 82–93% (38), 87% (137)) *N*-phenylanthranilic acid (diphenylamine-*o*-carboxylic acid) [Beil XIV-327, XIV$_1$-(533)], cryst. from alc., m.p. 182–183° rap. htg (38); this prod. with conc H_2SO_4 at 100° loses aq and ring-closes *(yields: 91–96% (38)) (138) (139) to acridone [Beil XXI-335, XXI$_1$-(312)], sublimable* yel. ndls., m p. 354° cor.

[For details on analogous reaction of $\bar{C}$ with *o*-toluidine (134) (135) (136) (140), *m*-toluidine (134) (141), *p*-toluidine (134) (135), α-naphthylamine (134) (135), β-naphthylamine (134) (135), *o*-aminophenol (134), *o*-anisidine (134), *m*-anisidine (134) (141), *p*-anisidine (142), *o*-aminobenzoic acid (134), *m*-aminobenzoic acid (134), *p*-aminobenzoic acid (134), *p*-phenylenediamine (134), *p*-aminodimethylaniline (124), see indic. refs.; scores of other examples cannot be cited here.]

Substitution of nucleus of $\bar{C}$. — [$\bar{C}$ in fumg. H_2SO_4 or chlorosulfonic acid + a little sulfur treated with Br_2 (1 mole) at 60–70° gives (70–75% yield (143)) 5-bromo-2-chlorobenzoic acid [Beil. IX-355], ndls , m.p. 165–167° (143).]

$\bar{C}$ on mononitration under various conditions, e g., $\bar{C}$ (2 wt pts) dislvd. in conc. H_2SO_4 (15 wt. pts) and treated below 50° with a mixt. of HNO_3 (D = 1 5) (1 wt. pt.) in conc. H_2SO_4 (2.5 wt pts) (144) gives mainly (yields: 78.5% (144), 35% (145), 32–38% (146)) (147) (148) (14) (149) 2-chloro-5-nitrobenzoic acid [Beil. IX-403], ndls. from aq., m.p. 165° (149) (14) (172), 164–165° (144) (145), 164° (146) (148), accompanied by a small amt. 2-chloro-3-nitrobenzoic acid [Beil IX-402], m p. 185° (148), 181° (150). — [Note that both the other nitro-2-chlorobenzoic acids are known, viz, 2-chloro-4-nitrobenzoic acid [Beil. IX-404], ndls. from aq , m.p. 140° (151), 139–140° (152), and 2-chloro-6-nitrobenzoic acid, m.p 161° (151), but are prepd. by other methods.]

$\bar{C}$ on direct dinitration, e.g., with conc. H_2SO_4 + KNO_3 at 100° (153) (154) or at 130° (155) or $\bar{C}$ with conc. H_2SO_4 + fumg. HNO_3 at 130–140° (156), gives (94% yield (155)) 2-chloro-3,5-dinitrobenzoic acid [Beil. IX-415], ndls from aq., m.p. 199–200° (153) (154), 199° (156), 198 5° cor. (155) (for use of this prod in detection of $\bar{C}$ see (180)); this prod. is also obtd. by further nitration of 2-chloro-3-nitrobenzoic acid (above) with conc. H_2SO_4 + KNO_3 at 170° (157) — [Note that of the 5 other isomeric dinitro-2-chlorobenzoic acids which are possible only one is known, viz., 2-chloro-4,5-dinitrobenzoic acid, m.p. 165° cor. (158), obtd. from 2-chloro-4-nitrobenzoic acid (above) by further nitration with fumg. HNO_3 + conc. H_2SO_4 (80% yield (158)).]

—— **Methyl *o*-chlorobenzoate**: oil, b.p. 234°. (See 3:6695.)

—— **Ethyl *o*-chlorobenzoate**: oil, b.p. 243°. (See 3:6800)

Ⓓ ***p*-Nitrobenzyl *o*-chlorobenzoate**: m.p. 106° (159). [From $\bar{C}$ (as Na$\bar{A}$) with *p*-nitrobenzyl bromide (m.p. 99°) in boilg. dil. alc. (159); note that the m.p. of this ester is almost identical with that (107°) of the corresp. prod. from *m*-chlorobenzoic acid (3·4392).]

Ⓓ **Phenacyl *o*-chlorobenzoate**: m.p. 85.5° (160), 83° (23). [From $\bar{C}$ (as Na$\bar{A}$) with phenacyl bromide (m.p. 50°) in boilg. alc. (97% yield (23)).] — [Note that the m.p. of this prod. is only slightly lower than that (87.6°) of the corresp. prod. similarly obtd from *p*-chlorobenzoic acid (3:4940).]

—— ***p*-Chlorophenacyl *o*-chlorobenzoate**: unreported.

Ⓓ ***p*-Bromophenacyl *o*-chlorobenzoate**: m.p. 107.0° cor. (161), 106° (23) (162). [From $\bar{C}$ (as Na$\bar{A}$) with *p*-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (23)).]

—— *p*-Iodophenacyl *o*-chlorobenzoate: unreported.

Ⓓ *p*-Phenylphenacyl *o*-chlorobenzoate: m.p. 123° (163). [From C̄ (as NaĀ) with *p*-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (163).]

—— *S*-Benzylthiuronium *o*-chlorobenzoate: unreported.

Ⓓ *S*-(*p*-Chlorobenzyl)thiuronium *o*-chlorobenzoate: cryst. from dioxane, m.p. 159° cor. (164). [From C̄ (as NaĀ or KĀ) in aq. with 1 equiv. of *S*-(*p*-chlorobenzyl)-thiuronium chloride, m.p. 197° (10% in alc.) (164); note that the m p. of this prod is closely adjacent to that (m.p. 157° cor.) of the corresp. salt of *m*-chlorobenzoic acid (3:4392).]

Ⓓ *S*-(*p*-Bromobenzyl)thiuronium *o*-chlorobenzoate: m.p. 168° cor. (165). [From C̄ (as KĀ or NaĀ) in aq. with 1 equiv. of *S*-(*p*-bromobenzyl)thiuronium bromide (m p. 213°) in alc. (165); note that m.p. of this prod. is only slightly higher than that (163° cor.) for the corresp. prod. from *p*-chlorobenzoic acid (3:4940).]

Ⓓ *o*-Chlorobenzamide: cryst. from alc. or alc./ether, m.p. 142.4° cor. (166), 142° (167), 141° (14), 140.5° (91), 139° (25). [From C̄ by refluxing with AcOH + $(NH_4)_2CO_3$ (37–39% yield (167)), from *o*-chlorobenzoyl chloride (3:6640) with conc. aq. NH_4OH (166) (14) (91) (25), or from ethyl *o*-chlorobenzoate (3:6800) with conc. aq. NH_4OH (25).] — [Note that *o*-chlorobenzamide on htg. with $AlCl_3.NaCl$ (large excess) gives (93% yield (168)) *o*-chlorobenzonitrile [Beil. IX-336], m.p. 43–44° (168), 42–43° (169), b.p. 232° (169).]

Ⓓ *o*-Chlorobenzhydrazide: ndls. from alc., m.p. 117–118° (170), 109–110° (171). [From ethyl *o*-chlorobenzoate (3:6800) q.v. with hydrazine hydrate (170) (171); for use as reagt. for identification of aldehydes and ketones see (170).]

—— *N*-(*o*-Chlorobenzoyl) *N*-phenylhydrazide: unreported.

Ⓓ *o*-Chlorobenzanilide: ndls. from alc. or pet. ether; m.p. 114° (172) (173) (174), 117–118° (175) (176). — [From *o*-chlorobenzoyl chloride (3:6640) with excess aniline (25) (172) in pres of a tertiary amine (80% yield (174)); also from oxime of *o*-chlorobenzophenone (3:0715) by Beckmann rearr. (175) (173) (176).] — [Note that this prod must not be confused with benz-*o*-chloroanilide, m.p. 99–100°.]

Ⓓ *o*-Chlorobenz-*p*-toluidide: cryst. from dil. alc., m.p. 131° (177). [From *o*-chlorobenzoyl chloride (3:6640) with *p*-toluidine (177).]

—— *o*-Chlorobenz-α-naphthalide: unreported.

—— *o*-Chlorobenz-β-naphthalide: unreported.

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(61) Neogi, Mitra, *J. Chem. Soc.* **1928**, 1332. (62) Atkinson, Holm-Hansen, Nevers, Marino, *J. Am. Chem. Soc.* **65**, 476 (1943). (63) Henry, *Ber* **2**, 492–493 (1869). (64) Britton (to Dow Chem. Co), U.S. 1,878,463, Sept. 20, 1932; *Cent.* **1933**, I 311; *C.A* **27**, 308 (1933). (65) M.L B , Ger. 229,873, Jan. 6, 1911; *Cent.* **1911**, I 358. (66) Anschütz, *Ann.* **454**, 99 (1927). (67) Heller (to Chem Fabrik von Heyden), Ger. 639,578, Dec. 8, 1936; *Cent.* **1937**, I 2025; *C.A.* **31**, 3943 (1937). (68) Claus, Bucher, *Ber.* **20**, 1623 (1887). (69) Lossen, Ger. 146,174, Nov. 6, 1903; *Cent.* **1903**, II 1224. (70) Jaeger (to Selden Co), U.S. 1,953,231 & 1,953,232, April 3, 1934; *Cent.* **1934**, II 669, 1688.

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Ber. **36,** 2382–2384 (1903).
(138) Graebe, Lagodzinski,

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(151) Lehmstedt, Schrader, *Ber.* **70,** 1536–1537 (1937). (152) Magidson, Grigorowski, *Ber.* **66,** 869 (1933). (153) Cohn, *Monatsh.* **22,** 386–387 (1901). (154) Kalle & Co., Ger. 106,510, Dec. 23, 1898; *Cent.* **1900,** I 742. (155) Ullmann, *Ann.* **366,** 82–83 (1909). (156) Purgotti, Contardi, *Gazz. chim. ital.* **32,** I 527–528 (1902). (157) Holleman, *Rec. trav. chim.* **20,** 235–236 (1901). (158) Goldstein, Studer, *Helv. Chim. Acta* **20,** 1409 (1937). (159) Reid, *J. Am. Chem Soc.* **39,** 132 (1917). (160) Chen, *Trans. Science Soc. China* **7,** 73–80 (1931).

(161) Lund, Langvad, *J. Am. Chem. Soc.* **54,** 4107 (1932). (162) Chen, Shih, *Trans. Science Soc. China* **7,** 81–87 (1931). (163) Kelly, Morisani, *J. Am. Chem. Soc.* **58,** 1502 (1936). (164) Dewey, Sperry, *J. Am. Chem. Soc.* **61,** 3251–3252 (1939). (165) Dewey, Shasky, *J. Am. Chem. Soc.* **63,** 3526–3527 (1941). (166) Remsen, Reed, *Am. Chem. J.* **21,** 289–290 (1899). (167) Kao, Ma, *Science Repts. Natl. Tsing Hua Univ.* **A-1,** 21–22 (1931). (168) Norris, Klemka, *J. Am. Chem. Soc.* **62,** 1432–1435 (1940). (169) Henry, *Ber.* **2,** 492–493 (1869). (170) Sun, Sah, *Science Repts. Natl. Tsing Hua Univ.* **A-2,** 359–363 (1934); *Cent.* **1935,** I 57; *C.A.* **29,** 466 (1935).

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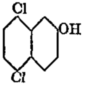
3:4155 5,8-DICHLORONAPHTHOL-2  $C_{10}H_6OCl_2$ **Beil. S.N. 538**

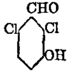
M.P. 141–142° (1)

[For prepn. from 5,8-dichloro-2-aminonaphthalene by htg. with dil. H_2SO_4 for 8 hrs. at 195–205° under pressure see (1) (2).]

—— **5,8-Dichloro-2-naphthyl methyl ether:** m.p. 74° (2).

3:4155 (1) Soc. Chem. Ind., Basel, Swiss 202,854, May 1, 1939; *Cent.* **1939,** II 3196. (2) Goldstein. Viaud, *Helv. Chim. Acta,* **27,** 883–888 (1944); *C.A.* **39,** 926 (1945).

3:4160 2,6-DICHLORO-3-HYDROXYBENZALDEHYDE $C_7H_4O_2Cl_2$ Beil. S.N. 745



M.P. 142–142.2° (1)
140.5° cor. (2) (3)
140° (4)

Colorless cryst. from hot aq — $\bar{C}$ has pronounced sternutatory properties and also attacks moist skin producing painful blisters. — [$\bar{C}$ when mixed with 2-chloro-3-hydroxybenzaldehyde (3:4085), m.p. 139.5° (4), depresses m p. to 116° (4)]

[For prepn. of $\bar{C}$ from *m*-hydroxybenzaldehyde (1·0055) with Cl_2 (2 moles) in AcOH soln. (yields: 51.5% (2) cf (3), 38% (4)) (1) (other prods. also being formed) see indic. refs ; from 2-chloro-3-hydroxybenzaldehyde (3:4085) with Cl_2 (1 mole) in AcOH see (4); from 6-chloro-3-hydroxybenzaldehyde (3:3350) with Cl_2 (1 mole) in AcOH ($\bar{C}$ is main prod (5) but 4,6-dichloro-3-hydroxybenzaldehyde (3:3952) is also formed (4) (5)) see indic refs]

[For condens of $\bar{C}$ with *p*-chlorophenol (3.0475) and use of prod. as mothproofing agent see (6); for condens. of $\bar{C}$ with 2,4-dihydroxybenzoic acid (1:0843) (7) or with *o*-cresotinic acid (2-hydroxy-3-methylbenzoic acid) (8) and use of products as dye intermediates see indic. refs]

$\bar{C}$ in 50% aq KOH at 60–70° first ppts yel. K salt of $\bar{C}$ which grad dissolves and is replaced by a colorless cryst. ppt.; after stdg. 4 hrs. acidification with dil. H_2SO_4 gives (93.8% yield (2)) 2,4-dichlorophenol (3·0560), m p. 42° (2).

$\bar{C}$ in AcOH with Br_2 gives (70% yield (3)) 4-bromo-2,6-dichloro-3-hydroxybenzaldehyde, cryst from C_6H_6 + lgr , m p. 104–105° (3) (methyl ether, m p 82°, oxime, m p. 193° cor. (3)).

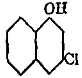
$\bar{C}$ (1 pt.) in AcOH (4 pts) on nitration with 1 pt. conc. HNO_3 (D = 1.42) at 65° yields (4) 2,6-dichloro-3-hydroxy-4-nitrobenzaldehyde, bright yel. ndls. from AcOH or pl. from aq , m p. 80° (4) (Ag salt, crimson ndls from hot aq ; oxime, deep yel. ndls. from dil. alc., m p. 195°; *p*-nitrophenylhydrazone, deep red ndls from hot AcOH, m.p 279–280° dec.; semicarbazone, light-yel. lfts. from hot alc , m p 255–256° (4)).

$\bar{C}$ dislvd in hot aq. $NaHCO_3$ and treated with Me_2SO_4 for 15 min yields (4) (3) the corresp. methyl ether, viz , 2,6-dichloro-3-methoxybenzaldehyde, m p. 103–104° (3), 102° (4) (*p*-nitrophenylhydrazone, old-gold ndls., m.p. 214–215° (4)); this methyl ether upon oxidn. with alk. $KMnO_4$ gives (4) 2,6-dichloro-3-methoxybenzoic acid, ndls. from dil. alc , m.p. 149 5° (4).

Ⓓ **2,6-Dichloro-3-hydroxybenzaldoxime:** ndls from dil. alc., m p. 174–175° (4).

Ⓓ **2,6-Dichloro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** deep or.-red. ndls., m p. 205–206° (4).

3:4160 (1) Bissell, Kranz (to National Aniline and Chem Co), U.S. 1,776,9[illegible] *Cent.* **1931**, I 159; *C.A* **24**, 5768–5769 (1930). (2) I[illegible] *Monatsh.* **62**, 184–185, 193–194 (1933). (4) Hodgs[illegible] 152–153, 155 (5) Hodgson, Beard, *J. Chem. Soc.* 1[illegible] Stötter (to I G), Ger. 530,219, July 24, 1931; *Cent.* [illegible] (7) Weiler (to F. Bayer & Co), U.S. 1,532,790, April 7, 1925; *Cent.* **1925**, II 352. (8) I.G., Brit. 263,879, March 2, 1927; *Cent.* **1927**, I 2364.

3:4170 3-CHLORONAPHTHOL-1  $C_{10}H_7OCl$ Beil. VI —
VI₁—
VI₂-(581)

M.P. 143° (1)
134–135° (2)

Ndls. from lgr. (2), C_6H_6, alc. or 80% AcOH (1). — Volatile with steam (1).

[For prepn. of C̄ from 3-chloronaphthylamine-1 (1) via diazotization and . . . of the diazonium salt with steam see (1); from 2,3,4-trichloronaphthol-1 [Beil. VI-613] by partial reduction with HI ($D = 1.7$) in AcOH on boilg. 7 hrs. (100% yield) see (2).]

C̄ is sol. in aq. alk., and the result. soln. couples with solns. of diazonium salts (1).

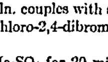
C̄ with Br_2 aq. (and alk.?) gives 3-chloro-2,4-dibromonaphthol-1, pr. from 90% formic acid, m.p. 112° (1).

[C̄ in 10% aq. KOH shaken with Me_2SO_4 for 20 min. gives (81% yield (2)) 3-chloronaphthol-1 methyl ether, oil, b.p. 162–164° at 18 mm. (2).]

Ⓓ **3-Chloro-1-naphthyl acetate:** ndls. from lgr., m.p. 69° (2). [From C̄ with acetyl chloride in C_6H_6 on refluxing 3 hrs. in C_6H_6 (66% yield (2)).]

Ⓓ **3-Chloro-1-naphthyl benzoate:** ndls. from lgr., m.p. 118–119° (2). [From C̄ in 10% aq. KOH on shaking with BzCl (71% yield (2)).]

3:4170 (1) Hodgson, Elliott, *J. Chem. Soc.* **1934**, 1707. (2) Franzen, Stäuble, *J. prakt. Chem.* (2) **103**, 385–387 (1922).

3:4200 2,6-DICHLOROBENZOIC ACID  $C_7H_4O_2Cl_2$ Beil. IX - 343
IX₁-(141)

M.P. 144° (1) (2)
143.7° (3)
143–144° (4)
141.5–142.5° (5)

Many recorded m.p.'s lower than these values [cf. . . . now known to have been impure.

Cryst. from lgr. (1) or mixt. of C_6H_6 + lgr. (4 . . . from alc. — Can also be purified by distn. in vac . . .

[For prepn. of C̄ from 2,6-dichlorotoluene (3 . . . to 2,6-dichlorobenzyl bromide, conversion to . . . $KMnO_4$ see (1) (4); from 2,6-dichlorobe . . . older less satisfactory methods see Beil. IX-343.]

C̄ on htg. begins to lose CO_2 at 235° (5). [C̄ . . . 150° for 24 hrs. was recovered unchanged to . . .

C̄ on nitration under stated conditions (1) gives . . . acid, cryst. from toluene, m.p. 152° (1).

C̄ (as KĀ) htd. with aniline + K_2CO_3 + Cu in . . . aminecarboxylic acid-2, cryst. from C_6H_6, m.p. 1 . . . atoms.]

C̄ htd. with acetamide for 6 hrs. at 225–235° . . . (3:5960), b.p. 172°.

C̄ htd. with PCl_5 (6) or with $SOCl_2$ + pyridine (4) . . . b.p. 142–143° at 21 mm. (6), 126–128° at 18 mm. (7).

—— Methyl 2,6-dichlorobenzoate: from $Ag\bar{A}$ + MeI (8); b.p. 250° (8).

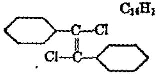
—— Ethyl 2,6-dichlorobenzoate: from $Ag\bar{A}$ + EtI (8) or from $\bar{C}$ via $SOCl_2$, followed by EtOH (82% yield (5)); cannot be prepared by direct esterification (8); b.p. 264–265° (8). [This ester on htg. with $AlCl_3$ at 120–130° for 2½ hrs. gives EtCl (91%) and $\bar{C}$ (92%) (5).]

⑩ 2,6-Dichlorobenzamide: ndls. from alc., m.p. 202° (8), 198° (7). [This amide htd. with $NaCl.AlCl_3$ over free flame evolves HCl and gives (67% yield (5)) 2,6-dichlorobenzonitrile, ndls. from lgr., m.p. 142.5–143.5° (5), 143° (9); the nitrile can be reconverted to the amide with alk. H_2O_2 (9).]

—— 2,6-Dichlorobenzanilide: unrecorded.

3:4200 (1) Lehmstedt, Schrader, *Ber* 70, 1530–1531 (1937). (2) Davies, *J. Chem. Soc.* 119, 873 (192[illegible] [illegible] 31, [illegible] (·) [illegible]orris, Bearse, *J. Am.* [illegible] 62, 1432–1435 (1940). [illegible] [illegible]uint, Heinen, *J. prakt* [illegible] 71. [illegible] (9) Ref. 8, pp. 222–223. (10) Lock, Böck, *Ber.* 70, 922 (1937).

3:4210 *trans*-1,2-DICHLORO-1,2-DIPHENYLETHYLENE (*trans*-α,α′-Dichlorostilbene; *trans*-tolane dichloride)



$C_{14}H_{10}Cl_2$ Beil. V - 634 V_1-(304) V_2—

M.P. [153°	(1)]	B.P. 316.5° cor. at 767 mm.	(20)	
[150°	(2)]	183° at 18 mm.	(6)	
[148°	(3)]			
143–144°	(4)			
143°	(5) (6) (7) (13)			
142.5°	(8)			
142–143°	(17)			
140–142°	(9)			
141°	(19)			
139–140°	(13)			
139.5°	(10)			
138–139°	(11)			

[*See also cis*-1,2-*dichloro*-1,2-*diphenylethylene* (3:1380).]

Colorless tbls. from alc.; $\bar{C}$ is much less sol. in alc. than its *cis* isomer (3:1380); 100 pts. abs. alc. at 24.4° dis. 0.71 pt. $\bar{C}$, but soly. of $\bar{C}$ is diminished by pres. of its stereoisomer (10). — $\bar{C}$ (like its isomer) is very sol. ether.

Note that $\bar{C}$ (the higher-melting tolane dichloride) has now been shown (4) to have the *trans* configuration, many earlier reports to the contrary notwithstanding.

Note also that $\bar{C}$ with 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496) gives an isomorphous mixt. (2), formerly erroneously regarded as an individual cpd. designated as "ditolane hexachloride."

PREPARATION OF $\bar{C}$

Note that in all processes (below) for prepn. of $\bar{C}$ more or less of the lower-melting (*cis*) stereoisomer is always formed.

FROM DINUCLEAR INITIAL MATERIALS

From diphenylacetylene (tolane). [For prepn. of $\bar{C}$ from tolane [Beil. V-656, V_1-(319), V_2-(568)] with Cl_2 in $CHCl_3$ see (7).]

From *trans*-1,2-diphenylethylene (stilbene). [For prepn. of $\bar{C}$ from stilbene (1:7250) with PCl_5 (2 moles) in $POCl_3$ at 170° see (12).]

From 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride). [For prepn. of $\bar{C}$ from tolane tetrachloride (3:4496) by removal of two adjacent chlorine atoms by use of Zn dust in EtOH (1) (6) (7) (10), Zn dust in AmOH (6), Fe powder in boilg. AcOH (14) (6) (note that in this method ratio of $\bar{C}$ to lower m.p. stereomer is 1:5 (6)), or by use of excess conc. (2 *N*) MeMgCl (11), or with H_2 + hydrazine hydrate in MeOH/KOH at b.p. for 1½ hrs. (3) see indic. refs.]

From benzoin. [For formn. of $\bar{C}$ from benzoin (1:5210) with PCl_5 at 0° (much benzoyl-phenyl-dichloromethane("chlorobenzil") [Beil. VII-436, VII_1-(234)] also being formed) see (20).]

FROM MONONUCLEAR INITIAL MATERIALS

From benzotrichloride. [For prepn. of $\bar{C}$ from benzotrichloride (3:6540) with Cu powder (yield of total mixed stereoisomers 68% (15), 23 5% (16) (17)), by action of excess conc. (2 *N*) MeMgCl (yield total mixed stereoisomers 22% (11)), by action of hydrazine hydrate + Pd in MeOH/KOH (35% yield (3)), or for formn. of $\bar{C}$ (together with other products) by pyrolysis over hot Pt (18) see indic. refs.]

From benzal (di)chloride. [For formn. of $\bar{C}$ (together with other prods.) from benzal (di)chloride (3:6327) by pyrolysis over hot Pt see (18).]

FROM MISCELLANEOUS SOURCES

[For formn. of $\bar{C}$ from CaC_2 with satd. soln. of Cl_2 in C_6H_6 see (13); from benzoyl-phenyl-diazomethane (azibenzil) [Beil. VII_1-(395), XXIV-208] with oxalyl (di)chloride (3:5060) in C_6H_6 (38.5% yield $\bar{C}$) see (9); from 1,1,2-trichloro-1,2-diphenylethane [Beil. V-601] by elimination of HCl with alc. KOH see (19); for formn. of $\bar{C}$ from its lower-melting stereoisomer (3:1380) by distn. (about 32% conversion to $\bar{C}$ (10)) (12) (6) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

$\bar{C}$ on htg is partially transformed (6) (12) to the lower-melting isomer (3:1380); on distn. conversion is about 68% (10).

Reduction of $\bar{C}$. $\bar{C}$ with conc. HI and red P in s.t. at 170° for 20 hrs. gives (16) (20) bibenzyl (1:7149), m.p. 52°.

Elimination of 2 chlorine atoms. $\bar{C}$ with Na/Hg in alc. (1) (16), or $\bar{C}$ with Zn dust in boilg. alc. (7) (10), or $\bar{C}$ with alc. KOH in s.t. at 180° (12) gives diphenylacetylene (tolane) [Beil. V-656, V_1-(319), V_2-(568)], m.p. 60°.

Addn. of halogens. $\bar{C}$ with Cl_2 in C_6H_6 soln. yields (13) 1,1,2,2-tetrachloro-1,2-diphenylethane (tolane tetrachloride) (3:4496). — $\bar{C}$ does *not* (12) add Br_2, and the expected prod. 1,2-dibromo-1,2-dichloro-1,2-diphenylethane is unreported from any other source.

Nitration of $\bar{C}$. The nitration of $\bar{C}$ has never been studied, and neither mono nor dinitro derivs. are reported from any other source.

3:4210 (1) Zinin, *Ber.* **4**, 288–289 (1871). (2) Marckwald, Karczag, *Ber.* **40**, 2994–2995 (1907). (3) Busch, Weber, *J. prakt. Chem.* (2) **146**, 50–52 ... **1936**, ... 405. (5) Arends, *Ber.* **64**, 1939 (1931). (6) ... (7) ... ann, Homeyer, *Ber.* **12**, 1973–1974 (1874). ... 4). Staudinger, *Ber.* **49**, 1971–1972 (1916). (10) ...

Am. Chem. Soc. 55, 723 (1933). (12) Limpricht, Schwanert, *Ber.* 4, 379
) (1916). (14) Lachowicz, *Ber.* 17, 1165
(2) 83, 115-116 (1911). (16) Hanhart,
(1884). (18) Loeb, *Ber.* 36, 3060-3061
897). (20) Redsko, *J. Russ. Phys-Chem.*

3:4220 2,3-DICHLOROHYDROQUINONE (2,3-Dichloroquinol; o-dichlorohydroquinone)

$C_6H_4O_2Cl_2$ Beil. VI - 849; VI_1—; VI_2-(845)

M.P. 144-145° (1)
144° (2) (3) (5)
143° (4)

[*See also* 2,3-*dichlorobenzoquinone*-1,4 (3:2885).]

Ndls. from aq. with 2 H_2O lost at 100° or over conc. H_2SO_4 (1); eas. sol. alc., insol. cold lgr ; sublimes.

[For prepn. of C̄ from hydroquinone (1:1590) in ether with SO_2Cl_2 (1) (6), in AcOH with Cl_2 (30% yield (4)) (7) (6), in ether with EtOCl (3), or in MeOH with Cl_2 (9) see indic. refs.; from chlorobenzoquinone (3:1100) in ether with HCl gas (12% yield (5)) ... sometimes fails (8) (6)); from

resultant diacetate (2)]

[For use as antioxidant and gum inhibitor in cracked gasoline see (10); in aq. petroleum emulsion as insecticidal oil spray see (11)]

C̄ with $FeCl_3$ gives a greenish black quinhydrone (1).

C̄ in AcOH with excess Br_2 yields (6) 4,5-dibromo-2,3-dichlorohydroquinone, golden-yel lfts from lgr , m p 294° (6).

C̄ reduces $NH_4OH/AgNO_3$ and Fehling's soln. (1); C̄ on oxidn. with MnO_2 + dil. H_2SO_4 (1) (4) (5) or with CrO_3/AcOH (7) gives (yields: 88% (4), 60% (1)) 2,3-dichlorobenzoquinone (3:2885) q.v [For study of oxidn -reductn. potential of C̄ see (4)]

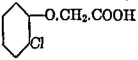
- Ⓓ **2,3-Dichlorohydroquinone diacetate:** colorless ndls. from dil. alc., m.p. 121° (6) (2). [From C̄ + Ac_2O (6), or from p-benzoquinone dichloride (see above) with Ac_2O + H_2SO_4, (2)]
- Ⓓ **2,3-Dichlorohydroquinone dibenzoate:** colorless cryst. from CS_2 or pet. ether, m p. 173-174° (1). [From C̄ in dil. aq alk. with BzCl (1).]
- Ⓓ **2,3-Dichlorohydroquinone dimethyl ether:** pinkish white ndls. from dil. alc., m p. 124° (6). [From C̄ in dil. alk with Me_2SO_4 (6)] [Note that corresp. deriv. of 2,5-dichlorohydroquinone (3:4690) has m.p. 125-127° but that a mixt. of the two derivs. is depressed to m p. 97° (6)]

3:4220 (1) ...

601 (1930).

(11) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* **1931**, I 2799; *C.A.* **24**, 5928 (1930).

3:4260 *o*-CHLOROPHENOXYACETIC ACID $C_8H_7O_3Cl$ Beil. VI — VI_1— VI_2-(172)



M.P. 147.2–147.7° cor. (4)
145–146° (1) (2) (3) **Neut. Eq. 186.5**

Wh. ndls. (from hot aq.). [For prepn. from *o*-chlorophenol (3:5980) by htg. with chloroacetic ac. (3:1370) and aq. alk. see (1) (2) (3).]

C̄ refluxed with 1½ pts. thionyl chloride for 1½ hrs. gives (90% yield (1)) *o*-chlorophenoxyacetyl chloride, b.p. 136° at 12 mm., m.p. 18 4° (1).

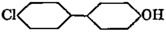
The methyl ester (b p. 186–188°) and the ethyl ester, ndls. (from alc.), m.p. 32°, have been prepd. from the acid chloride (1) (5)

o-Chlorophenoxyacetamide: from the acid chloride by treatment with excess $(NH_4)_2CO_3$; ndls. readily sol. in hot aq., alc., or C_6H_6, m.p. 149.5° (1).

o-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in C_6H_6; ndls (from alc.), m.p. 121° (1).

3:4260 (1) Minton, Stephen, *J. Chem. Soc* **121**, 1599–1601 (1922). (2) Behaghel, *J. prakt. Chem.* **114**, 297–298 (1926). (3) Koelsch, *J. Am. Chem. Soc.* **53**, 304–305 (1931). (4) Hayes, Branch, *J. Am. Chem. Soc.* **65**, 1555–1564 (1943). (5) Bacher, Raiford, *Proc. Iowa Acad. Sci.* **50**, 247–251 (1943), *C.A.* **38**, 2327 (1944).

3:4262 4-(*p*-CHLOROPHENYL)PHENOL $C_{12}H_9OCl$ Beil. VI — VI_1— VI_2-(625)
(4′-Chloro-4-hydroxybiphenyl)



M.P. 146–147° (1)
145.5–146° (3)
145–146° (2)

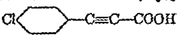
[C̄ is best prepd (nearly quant. yield (2)) by alk. hydrolysis of its acetate (see below) or by similar treatment (67% yield (3)) of its benzoate (see below) or (39% yield (3)) of its benzenesulfonate (see below); for formn. of C̄ from 4-amino-4′-hydroxybiphenyl by diazotization, etc., see (1); from 4′-chloro-4-aminobiphenyl (2) by diazotization and hydrolysis see (2).]

C̄ on chlorination with Cl_2 in CCl_4 soln. gives (92% yield (4)) 2-chloro-4-(*p*-chlorophenyl)phenol, m.p. 71–72° (corresp. acetate, m.p. 74 5–75°; corresp benzoate, m.p. 125–126°; corresp. benzenesulfonate, m.p. 100–101°) (4).

- Ⓓ **4-(*p*-Chlorophenyl)phenyl acetate:** m p 113° (2) [From C̄ by acetylation, or from the acetate of 4-hydroxybiphenyl (1:1585) with Cl_2 in CCl_4 + trace of I_2 (47% yield (2)) or similarly in AcOH (5).] [Note that the m.p. of this prod. has also been given without details of prepn. as 72° (6).]
- Ⓓ **4-(*p*-Chlorophenyl)phenyl benzoate:** m.p. 182° (3). [From C̄ by benzoylation or from the benzoate of 4-hydroxybiphenyl (1:1585) with Cl_2 in CCl_4 soln. + trace of I_2 (55% yield (3)).]
- Ⓓ **4-(*p*-Chlorophenyl)phenyl benzenesulfonate:** m.p. 74–75° (3). [From C̄ with benzenesulfonyl chloride + aq. 10% NaOH (3), or from the benzenesulfonate ester of 4-hydroxybiphenyl (1:1585) with Cl_2 in CCl_4 soln. + trace I_2 (21% yield (3)).]

3:4262 (1) Angeletti, Gatti, *Gazz. chim. ital.* 58, 633 (1928). (2) Savoy, Abernathy, *J. Am. Chem. Soc* 64, 2219–2221 (1942). (3) Savoy, Abernathy, *J. Am. Chem. Soc.* 64, 2719–2720 (1942). (4) Savoy, Abernathy, *J. Am. Chem. Soc* 65, 1464–1465 (1943). (5) Schmidt, Savoy, Abernathy, *J. Am. Chem. Soc* 65, 296–297 (1943). (6) Hodgson, *J. Chem. Soc.* 1942, 583.

3:4265 *p*-CHLOROPHENYLPROPIOLIC ACID $C_9H_5O_2Cl$ **Beil. S.N. 950**



M.P. 147° (1)

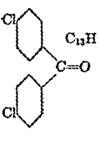
Cryst. from AcOH.

[For prepn. of C̄ from *p*-chlorobenzaldehyde (3:0765) by conversion through *p*-chlorocinnamic acid to ethyl *p*-chlorocinnamate, thence by addn. of Br_2 to give ethyl β-(*p*-chlorophenyl)-α,β-dibromopropionate, followed by elimination of 2 HBr and saponification (or vice versa) with alc. KOH, and final acidification (yield not stated), see (1).]

C̄ with $Cu(OAc)_2$ loses CO_2 yielding (1) *p*-chlorophenylacetylene (3:0590) (cf. also under *o-chlorophenylpropiolic acid* (3:3956))

3:4265 (1) Wilson, Wenzke, *J. Am. Chem. Soc.* 57, 1265–1267 (1935).

3:4270 4,4′-DICHLOROBENZOPHENONE (Di-*p*-chlorophenyl ketone) $C_{13}H_8OCl_2$ **Beil. VII - 420 VII₁-(228)**



M.P. 148°	(1)	**B.P. 353° at 757 mm.**	(2)
147.75°	(2) (20)	**243° at 38 mm.**	(15)
147°	(19)		
146.5–147.5° cor.	(40)		
146°	(3) (37)		
145°	(4) (5) (6) (7) (8) (16)		
144–145°	(9) (10)		
144.5°	(11) (14)		
144°	(12)		
142–143°	(13) (22)		

Colorless lfts. from alc ; eas. sol. ether, acetone, AcOH, $CHCl_3$, CS_2 — [For f.p./compn. data on systems C̄ + benzophenone (1:5150) and C̄ + diphenylamine see (12).]

[For prepn. of C̄ from *p*-chlorobenzoic acid (3·4940) + chlorobenzene (3:7903) + $AlCl_3$ (82% yield (1)) or from *p*-chlorobenzoyl chloride (3:6550) + chlorobenzene (3:7903) + $AlCl_3$ in CS_2 *in direct sunlight* (yields: 90% (17), 75–80% (2), 36% (9)) (37) (some isomeric 2,4′-dichlorobenzophenone (3:1565) also being formed) *see indic. refs.*; from chlorobenzene (3:7903) + $AlCl_3$ + CO_2 at 80–150° and 10 atm. press. (*p*-chlorobenzoic acid is main prod.) see (18); from *p*-chlorophenyl MgCl + CO_2 (together with *p*-chlorobenzoic acid) see (8).]

[For prepn. of C̄ from dichloro-*bis*-(*p*-chlorophenyl)methane (4,4′-dichlorobenzophenone

dichloride) (see below) by hydrolysis with boilg. dil. alc. (14) or conc. H_2SO_4 (14) (15) (6) (19) see indic. refs.; from tetra-(*p*-chlorophenyl)ethylene glycol (see below) on fusion or on boilg. with AcOH see (20); from 4,4′-dibromobenzophenone with PCl_5 at 150° see (21); from 4,4′-dichloro-3-nitrobenzophenone (see below) via reduction to amine, diazotization, and treatment with $SnCl_2$ + NaOH see (2).]

[For formn. of $\bar{C}$ by oxidation with CrO_3/AcOH of 4,4′-dichlorobenzilic acid (2), of *bis*-(*p*-chlorophenyl)methane (7), of *tris*-(*p*-chlorophenyl)methane (16), of 1,1,4,4-tetra-(*p*-chlorophenyl)butyne-2 (91% yield (4)), or of 1,1,4,4-tetra-(*p*-chlorophenyl)butatriene-1,2,3 (94% yield (5)) see indic. refs.; from oxidn. of β,β-di-(*p*-chlorophenyl) [illegible] with aq. $KMnO_4$ see (10); from [illegible] (*p*,*p*′-dichlorobenzohydryl)pinacolone [illegible] (*p*-chlorophenyl)propiophenone by oxidn. with aq. $KMnO_4$ in NaOH + pyridine soln. see (13); from *bis*-(*p*-chlorophenyl)methyleneacetophenone with $KMnO_4$ in acetone (71% yield) see (3).]

[For formn. of $\bar{C}$ from 1,1-di-(*p*-chlorophenyl)ethane (3:0995) (39), from 1-chloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:1430) (84% yield (40)), or from 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:2438) (40), all by oxidn. with CrO_3/AcOH, see indic. refs.]

[$\bar{C}$ on reduction with 3% Na/Hg in 90% alc. (20), with Al/Hg in 80% alc (6) (11), with Zn dust + AcOH on boilg. (20), with Zn dust + alc. KOH (20) or NaOH (23), or simply with boilg alc. KOH (24) gives (yields: 100% (23), 96% (6) (11)) di-(*p*-chlorophenyl)carbinol (4,4′-dichlorobenzhydrol) [Beil. VI-680, VI_1-(327)], cryst. from alc, m.p. 94° (20), 93° (24), 91.5° (23), 89–90° (6) (11) (corresp. 3,5-dinitrobenzoate, m.p. 174–176° (41)); note that in some cases this main prod. is accompanied by tetra-(*p*-chlorophenyl)ethylene glycol (see below). — $\bar{C}$ on reduction with Zn dust + AcOH + dil. H_2SO_4 (25), or in alc. in bright sunlight for 5 days (20) cf. (26), gives (85% yield (20)) tetra-(*p*-chlorophenyl)ethylene glycol [Beil. VI-1058, VI_1-(523)], m.p. 180° (6) (11), 175° (20) (accompanied by smaller amts. of other prods.).]

[$\bar{C}$ with sodium phenylacetylene in dry ether gives (57% yield (3)) *bis*-(*p*-chlorophenyl)-ethynyl-carbinol, m.p. 163–164° (3); $\bar{C}$ with diphenylmethyl sodium gives (27) *bis*-(*p*-chlorophenyl)-diphenylmethyl-carbinol, m.p. 183–184° (27); $\bar{C}$ with MeMgI in dry ether gives (39) (19) not only some *bis*-(*p*-chlorophenyl)-methyl-carbinol, m.p. 67.0–68.5° (39), but also (68% yield (19)), by loss of H_2O, *unsym.*-di-(*p*-chlorophenyl)ethylene, m.p. 91° (3:2475); $\bar{C}$ with β-(diphenylvinyl)MgBr gives (12% yield (28)) 1,1-di-(*p*-chlorophenyl)-3,3-diphenylpropen-2-ol-1, m.p. 85°, which on htg. at 130–150° loses H_2O yielding 1,1-di-(*p*-chlorophenyl)-3,3-diphenylpropadiene-1,2, m.p. 93–95° (28); $\bar{C}$ with ethyl bromoacetate + Zn in C_6H_6 gives (30% yield (28) ethyl β,β-di-(*p*-chlorophenyl)-β-hydroxypropionate, m.p. 102° (28).]

[$\bar{C}$ with PCl_5 at 150° gives (17) (15) (29) dichloro-di-(*p*-chlorophenyl)methane (4,4′-dichlorobenzophenone dichloride), m.p. 52–53° (15), 52.5° (17).]

[$\bar{C}$ on fusion with NaOH yields (7) chlorobenzene (3:7903) + *p*-chlorobenzoic acid (3:4940). — $\bar{C}$ with 10% aq. NaOH in pres. of Cu 5 hrs. at 190° under press. yields (30) 4,4′-dihydroxybenzophenone [Beil. VIII-317, $VIII_1$-(641)], m.p. 214° (30).]

[$\bar{C}$ with hydrazine hydrate in isopropyl alc. in s.t. at 150–160° for 7 hrs. gives (56% yield (42)) 4,4′-dichlorobenzophenone hydrazone, m.p. 91–93°, which on Wolff-Kishner reduction gives (21% yield (42)) 4,4′-dichlorodiphenylmethane (3:1057).]

[$\bar{C}$ with aq. NH_4OH in pres. of CuO + NH_4NO_3 + $KClO_3$ under press. at 180° (1) cf. (31) gives (92% yield (1)) 4,4′-diaminobenzophenone [Beil. XIV-88, XIV_1-(391)], m.p. 245–246° (1), 242.5° (31); some half reactn. prod., viz., 4-amino-4′-chlorobenzophenone, m.p. 185° (1), is also formed. — For similar reactn. of $\bar{C}$ with diethylamine leading to 4-chloro-4′-diethylaminobenzophenone see (32). — For reactn. of $\bar{C}$ with *N*-methyl-α-

phenylindole and use in prepn. of dyes see (33); with ethylbutyl-*m*-toluidine see (34); with aminoanthraquinone derivs. see (35) (36).]

[C̄ on nitration with 10 wt. pts. fumg. HNO_3 (D = 1.47) in cold (37) or with 5 pts. abs. HNO_3 at 0° (2) gives (81% yield (37)) 4,4′-dichloro-3,3′-dinitrobenzophenone, cryst. from AcOH, m p. 132.5° (2), 132–133° (38), 120° (37); C̄ on trinitration at 130° with 1.8 wt. pts. conc. H_2SO_4 contg. 2 pts. KNO_3 gives (37) 4,4′-dichloro-3,3′,5-trinitrobenzophenone, cryst. from AcOH, m.p. 140° (37); C̄ on tetranitration with 10 pts. fumg. H_2SO_4 + 1 pt. KNO_3 at 150° gives (37) 4,4′-dichloro-3,3′,5,5′-tetranitrobenzophenone, cryst. from AcOH, m.p. 202° (37).] [A *mono*-nitrated C̄, viz., 4,4′-dichloro-3-nitrobenzophenone. ndls. from alc , m.p. 87° (2), 88–89° (38) has been obtd. indirectly.]

Ⓓ **4,4′-Dichlorobenzophenone oxime:** ndls. from alc., m.p. 136–136.5° (1), 136° (7), 135° (8) (9), 134° (5). [From C̄ with excess NH_2OH in alc. at 100° (9)] [This prod. by Beckmann rearr. with conc. H_2SO_4 yields *p*-chlorobenz-*p*-chloroanilide, m.p. 213–213.5° (1).]

—— **4,4′-Dichlorobenzophenone phenylhydrazone:** not reported.

—— **4,4′-Dichlorobenzophenone *p*-nitrophenylhydrazone:** not reported.

—— **4,4′-Dichlorobenzophenone 2,4-dinitrophenylhydrazone:** m.p. 238–240° (40).

3:4270 (1) Newton, Groggins, *Ind. Eng. Chem* **27**, 1397–1399 (1935). (2) Montagne, *Rec. trav. chim.* **21**, 24–29 (1902). (3) Meyer, Schuster, *Ber.* **55**, 822–823 (1922). (4) Brand, Horn, Bausch, *J. prakt. Chem.* (2) **127**, 246–247 (1930). (5) Brand, Bausch, *J. prakt. Chem.* (2) **127**, 235–236 (1930). (6) Cohen, Böeseken, *Rec. trav. chim.* **38**, 115–116, 123 (1919). (7) Stephen, Short, Gladding, *J. Chem. Soc.* **117**, 523 (1920). (8) Bodroux, *Bull. soc. chim* (3) **31**, 29 (1904). (9) Dittrich, *Ann.* **264**, 175–178 (1891). (10) Fuson, Kozacik, Eaton, *J. Am. Chem. Soc.* **55**, 3803 (1933).

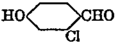
(11) Böeseken, Cohen, *Cent.* **1915**, 1375–1376. (12) Schaum, Rosenberger, *Z. anorg allgem. Chem.* **136**, 335–336 (1924). (13) Eaton, Black, Fuson, *J. Am. Chem. Soc.* **56**, 688 (1934). (14) Norris, Green, *Am. Chem. J.* **26**, 496–497 (1901). (15) Norris, Twieg, *Am. Chem. J.* **30**, 398 (1903). (16) Fischer, Hess, *Ber.* **38**, 337–338 (1905). (17) Montagne, *Rec. trav. chim.* **25**, 384, 389 (1906). (18) I.G., Brit. 307,223, March 28, 1929; *Cent.* **1929**, I 3145; Meyer, Hopff (to I.G.), Ger. 524,186, May 11, 1931; *Cent.* **1931**, II 497. (19) Bergmann, Bondi, *Ber.* **64**, 1469–1470 (1931). (20) Montagne, *Rec. trav. chim.* **24**, 114–120 (1905).

(21) Cone, Robinson, *Ber.* **40**, 2160–2161 (1907). (22) Weinstock, Fuson, *J. Am. Chem. Soc.* **56**, 1242 (1934). (23) Norris, Tibbetts, *J. Am. Chem. Soc.* **42**, 2091 (1920). (24) Montagne, Moll van Charante, *Rec. trav. chim.* **31**, 313–314 (1912). (25) Montagne, *Rec. trav. chim.* **25**, 411–414 (1906). (26) Cohen, Böeseken, *Rec. trav chim.* **39**, 258 (1920). (27) Bergmann, *J. Chem. Soc.* **1936**, 412–413. (28) Bergmann, Hoffmann, Meyer, *J. prakt. Chem.* **135**, 255, 261 (1932). (29) Schönberg, Schutz, *Ber.* **62**, 2331 (1929). (30) Britton (to Dow Chem. Co), U.S. 1,961,630, June 5, 1934; *Cent.* **1934**, II 1846; *C.A.* **28**, 4744 (1934).

(31) Britton, Bryner (to Dow Chem. Co.), U.S. 1,946,058, Feb. 6, 1934; *Cent.* **1934**, I 3396; *C.A.* **28**, 2364 (1934). (32) Hammond, Harris (to Heyden Chem. Co), U.S. 2,223,517, Dec. 3, 1940; *C.A.* **35**, 1808 (1941). (33) Wolff (to I G.), Brit. 417,014, Oct. 25, 1934; Ger. 604,429, Oct. 20, 1934; French 761,372, March 17, 1934; Swiss 170,094, Sept. 11, 1934; *Cent.* **1935**, I 801. (34) Wolff, [illegible]
Ger. 220,579, Ap [illegible]
574,966, April 21, [illegible]
(38) Maron, Fox, [illegible]
2266 (1945). (4[illegible]
J. Am. Chem. Soc. **67**, 1599, 1602 (1945).

(41) Grummitt, Buck, *J. Am. Chem. Soc.* **67**, 693–694 (1945). (42) Grummitt, Jenkins, *J. Am. Chem. Soc.* **68**, 914 (1946).

3:4280 2-CHLORO-4-HYDROXYBENZ-ALDEHYDE $C_7H_5O_2Cl$ Beil. VIII - 81
$VIII_1$—



M.P. 147–148° (1)
146.5° (2)

Colorless ndls. from AcOH (1) or aq. (2). — Volatile with steam but much less so than the isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) (1).

[For prepn. of C̄ from *m*-chlorophenol (3:0255) via Reimer-Tiemann reactn. see (1); via anhyd. HCN + $AlCl_3$ + C_6H_6 (50% yield) see (2); for prepn. (alm. 100% yield (1)) from 2-chloro-4-nitrotoluene via 2-chloro-4-aminotoluene and subsequent diazo reactn. see (1).]

C̄ does not reduce $NH_4OH/AgNO_3$ or Fehling soln. (1).

C̄ with aq. $FeCl_3$ gives only a slight ppt. [dif. from 4-chloro-2-hydroxybenzaldehyde (3:0960)]; the copper and chromium salts are lighter green in color than those from that isomer (1).

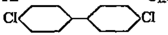
C̄ on mononitration as specified (3) yields 5-nitro-2-chloro-4-hydroxybenzaldehyde, vol. with steam, colorless ndls. from alc., m.p. 125° (3). [This product yields a phenylhydrazone, silky dark purple ndls. from alc., m.p. 166° sl. dec.; a *p*-nitrophenylhydrazone, deep or. ndls. from AcOH, m.p. 266° dec.; and a semicarbazone, light or. ndls. from dil. AcOH, m.p. 266° dec. (3).]

C̄ on dinitration as specified (3) yields 3,5-dinitro-2-chloro-4-hydroxybenzaldehyde, not volatile with steam, pale yel. massive pr. from aq., m.p. 93° (3). [This product yields a phenylhydrazone, br.-purple ndls. from alc., m.p. 210° dec.; a *p*-nitrophenylhydrazone, red-br. ndls. from dil. AcOH, m p. 267° dec ; and a semicarbazone, lt. br. ndls. from dil. AcOH, m.p. 192° dec. (3).]

Ⓓ **2-Chloro-4-hydroxybenzaldoxime:** cryst. from alc., m.p. 194° (2).
—— **2-Chloro-4-hydroxybenzaldehyde phenylhydrazone:** unrecorded.
Ⓓ **2-Chloro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone:** dark red pl. from alc. or vermilion red cryst. from AcOH, m.p. 288° dec. (1).
—— **2-Chloro-4-hydroxybenzaldehyde 2,4-dinitrophenylhydrazone:** unrecorded.
Ⓓ **2-Chloro-4-hydroxybenzaldehyde semicarbazone:** yel. cryst. from alc., m p. 214° (1).
Ⓓ **2-Chloro-4-acetoxybenzaldehyde:** colorless ndls. from dil. AcOH, m.p. 51.5° (1).
Ⓓ **2-Chloro-4-benzoxybenzaldehyde:** colorless ndls. from alc., m p. 96.5° (1). [Note that this Ⓓ does not give good distinction from isomeric 4-chloro-2-hydroxybenzaldehyde (3:0960) whose corresponding benzoate has m.p. 98.5° (1).]

3:4280 (1) Hodgson, Jenkinson, *J. Chem. Soc.* **1927**, 1740–1742. (2) Gattermann, *Ann.* **357**, 334 (1907). (3) Hodgson, Jenkinson, *J. Chem Soc.* **1928**, 2274–2275.

3:4300 4,4′-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ Beil. V - 579
V_1-(273)
V_2-(484)



M.P. 148–149° cor. (1) (2)
147.5–148.5° (3)
148° (4) (5) (6) (7) (8) (15) (17)
147–148° (9) (10) (18)
146.5–147° (11)
144–145° (12)

B.P. 315–319° (13)
315° (15) (17)

Colorless cryst. from toluene + lt. pet. (2), from 50% AcOH (14), or from alc. (11).

[For prepn. of C̄ from 4,4′-diaminobiphenyl (benzidine) [Beil. XIII-214, $XIII_1$-(58)] via tetrazotization and use of Cu powder (9), Cu_2Cl_2 (3), or $HgCl_2$ complex (82% yield (10)), see indic. refs.; from biphenyl (1:7175) in AcOH with Cl_2 (41% yield (2)) (convenient for prepn. small amts C̄) see (2); from 4,4′-dinitrobiphenyl with $SOCl_2$ in s t. for 10 hrs. at 200–210° see (7); from *p*-chloroiodobenzene [Beil. V-221, V_1-(119)] with Cu powder at 200–250° (82% yield) see (15).]

[For formn. of C̄ from chlorobenzene (3:7903) by pyrolysis see (16) (12) (for discussion of formn during mfg. of phenol from chlorobenzene see (19)); from biphenyl (1:7175) with Cl_2 in pres. of $SbCl_5$ (17) or I_2 (13) see indic. refs ; from 4,4′-dihydroxybiphenyl (1:1640) with PCl_5 see (13); from 4,4′-dichlorobiphenyl-3,3′-dicarboxylic acid on htg. see (18); from 4,4′-dichloro-3,3′-diaminobiphenyl via tetrazotization and htg. with alc. see (14), from decompn. of *bis*-(*p*-chlorobenzoyl) peroxide on htg see (6).]

[For manuf. of C̄ or mixts of dichlorobiphenyls contg. C̄ from biphenyl with Cl_2 see (20) (21) (22) (23); for use as insecticide see (24).]

[C̄ htd. under press. with conc. aq NH_4OH in pres of Cu_2Cl_2 and $Ca(OH)_2$ gives (99.5% yield (25)) 4,4′-diaminobiphenyl (benzidine); C̄ with aq. over Cu + silica gel at 525–600° gives (26) 4,4′-dihydroxybiphenyl (1:1640).]

C̄ on mononitration in 15 pts AcOH with 10 pts. HNO_3 (D = 1.46) at 100° for ½ hr. (2), or in nitrobenzene soln. with HNO_3 (D = 1.52) as directed (2), gives alm. quant. yield of 4,4′-dichloro-2-nitrobiphenyl, cryst. from alc or CCl_4, m.p. 102° (2) (27). [This prod. does *not* react with piperidine (27).]

C̄ on dinitration by soln in 7½ pts HNO_3 (D = 1 52) in an ice bath gives (2) mixt. contg. 81.3% 4,4′-dichloro-2,3′-dinitrobiphenyl and 18.7% 4,4′-dichloro-2,2′-dinitrobiphenyl By recryst. from AcOH 4,4′-dichloro-2,3′-dinitrobiphenyl is obtd. in ndls., m p. 141–142° (2), 140° (28), which on warming with piperidine for a few seconds yields (28) 4-chloro-4′-piperidino-2,3′-dinitrobiphenyl, or. ndls from alc., m p. 132° (28) (note that the principal dinitration prod. of C̄ is the 2,3′-dinitro-C̄ and *not* the 2,2′-isomer as formerly (29) supposed). — From the mother liq. of the above dinitration may be obtd. (2) the true 4,4′-dichloro-2,2′-dinitrobiphenyl, m.p. 138–139° (2); this does not react with piperidine.

C̄ on trinitration with 10 pts HNO_3 (D = 1.52) for 2 hrs. at 100° gives (2) (30) 4,4′-dichloro-2,3′,5′-trinitrobiphenyl, ndls. from AcOH, m.p. 166–167° (2), 164–165° (30); this prod warmed with piperidine gives 4-chloro-4′-piperidino-2,3′,5′-trinitrobiphenyl, crimson pr. from AcOH, m p. 182° (2).

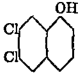
C̄ on oxidn. with CrO_3 in AcOH yields (13) *p*-chlorobenzoic acid (3:4940), m p. 237° (13).

3:4300 (1) Williamson, Rodebush, *J. Am. Chem. Soc.* **63**, 3019 (1941). (2) Shaw, Turner, *J. Chem. Soc.* **1932**, 288–289, 294–296. (3) Bretscher, *Helv. Phys. Acta* **1**, 358 (1928). (4) Griess, *J. Chem Soc.* **20**, 101 (1867). (6) Fichter, Adler, *Helv. Chim. Acta* **9**, 285 (1926). (7) 59, 870 (1929). (8) Brüll, *Gazz. chim. ital.* **65**, 21 (1935) ...sik. Chem. **B-3**, 309 (1929). (10) Schwechten, *Ber* **65**, 1607 (1932).

(11) Pickett, Walter, France, *J. Am Chem Soc.* **58**, 2296 (1936). (12) Meyer, Hofmann, *Monatsh.* **38**, 143 (1917). (13) Schmidt, Schultz, *Ann* **207**, 338–341 (1881). (14) Hodgson, Holt, *J. Chem Soc* **1934**, 1432 (15) Ullmann, *Ann.* **332**, 54–55 (1904). (16) Kramers, *Ann.* **189**, 137–140 (1877). (17) Kramers, *Ann.* **189**, 142–145 (1877). (18) Schultz, Rohde, Vicari, *Ann.* **352**, 130 (1907). (19) Hale, Britton, *Ind. Eng Chem.* **20**, 122 (1928). (20) Malowan (to Swann Research, Inc), U.S. 1,951,577, March 20, 1934; *Cent.* **1934**, II 3163; *C.A.* **28**, 3127 (1934).

(21) Federal Phosphorus Co., French 703,216, April 27, 1931; *Cent.* **1931**, II 1635. (22) Britton, Stoesser (to Dow Chem. Co), U.S. 1,835,754, Dec. 8, 1931; *Cent.* **1932**, I 1110. (23) Prahl, Mathes (to F. Raschig), Ger. 580,512, July 13, 1933; *Cent.* **1933**, II 1763. (24) I.G.,

Ger. 513,775, Dec. 2, 1930; *Cent.* **1931**, I 1965. (25) Booth (to Swann Research, Inc), U S. 1,954,469, April 10, 1934; *Cent.* **1934**, II 1846; *C.A.* **28**, 3744 (1934); Federal Phosphorus Co, Brit. 370,774, May 4, 1932; *Cent.* **1932**, II 1237. (26) Booth (to Swann Research, Inc.), U.S. 1,925,367, Sept. 5, 1933; *Cent.* **1934**, I 128; *C.A.* **27**, 5342 (1933). (27) LeFevre, Turner, *J. Chem. Soc.* **1926**, 2045 (28) Dennett, Turner, *J. Chem. Soc.* **1926**, 477, 479–480. (29) Borsche, Scholten, *Ber.* **50**, 609 (1917). (30) Vernon, Rebernak, Ruwe, *J. Am. Chem. Soc.* **54**, 4456–4457 (1932).

3:4315 6,7-DICHLORONAPHTHOL-1  $C_{10}H_6OCl_2$ **Beil. VI-613**
VI_1—
VI_2—

M.P. 151° (1) (2)
149–150° (3)

Cryst. from $CHCl_3$ (3).

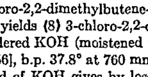
[For prepn. from β-(3,4-dichlorobenzal)propionic ac. [Beil. IX-614] by distn. see (1) (2) (3); C̄ is sepd. from the smaller proportion of 7,8-dichloronaphthol-1 (3:2635) by the greater soly. of the latter in lgr. (3).]

C̄ on oxidn. with $K_2Cr_2O_7$ + dil. H_2SO_4 yields (3) 4,5-dichlorophthalic ac. (3:4890), which during m.p. detn. is converted to 4,5-dichlorophthalic anhydride (3:4830), m.p. 184–185° (3).

C̄ in alk. soln. coupled with diazotized naphthionic acid (1-aminonaphthalenesulfonic acid-4) gives a deep red-bluish color which upon acidification becomes dark yellow (3). [Dif. from 7,8-dichloronaphthol-1 (3:2635) q.v.]

Ⓓ **6,7-Dichloro-1-naphthyl acetate:** ndls. from dil. alc., or compact pr. from $CHCl_3$ lgr., m.p. 102–103° (3).

3:4315 (1) Armstrong, Wynne, *Chem. News* **71**, 253 (1895). (2) Armstrong, Wynne, *Proc. Chem. Soc.* **11**, 78–79 (1895); *Ber.* **29**, Referate, 223–224 (1896). (3) Erdmann, Schwechten, *Ann.* **275**, 286–288 (1893).

3:4325 3,3-DICHLORO-2,2-DIMETHYLBUTANE  $C_6H_{12}Cl_2$ **Beil. I-150**
I_1—
I_2-(113)

M.P. 151–152° (1)

Colorless cryst. subliming readily even at ord. temp.

[For prepn of C̄ from *ter*-butyl methyl ketone (pinacolone) (1:5425) with PCl_5 at 0–5° (1) (2) (3) (4) (5) (6) (7) (9) see indic. refs. Note that C̄ (by loss of HCl) is always accompanied by more or less 3-chloro-2,2-dimethylbutene-3 (3:7340) and other prods.]

C̄ on htg. with phenol + KOAc yields (8) 3-chloro-2,2-dimethylbutene-3 (3:7340).

C̄ on htg. at 150–230° with powdered KOH (moistened with alc.) gives (65% yield (6)) (9) (2) *ter*-butylacetylene [Beil. I-256], b.p. 37.8° at 760 mm., $D_0^{20} = 0.6683$, $n_\alpha^{20} = 1.37257$ (6); note that use of NaOH instead of KOH gives by loss of 1 HCl only 3-chloro-2,2-dimethylbutene-3 (3:7340) and no *ter*-butylacetylene (9).

3:4325 (1) Bartlett, Rosen, *J. Am. Chem Soc.* **64**, 544 (1942). (2) Delacre, *Bull. soc. chim.* (3) **35**, 343–344 (1906). (3) Favorskii, *J. Russ. Phys.-Chem. Soc.* **19**, 425 (1887); *Ber.* **20**, Referate 781 (1887) (4) Delacre, *Bull acad. roy Belg.* **1906**, 7–41; *Cent.* **1906**, I 1233–1234. (5) Delacre, *Cent* **1906**, II 496. (6) Ivitzky, *Bull. soc. chim.* (4) **35**, 357–358 (1924). (7) Meerwein, Wortman, *Ann.* **435**, 201, Note 4 (1924). (8) Meerwein, Wortman, *Ann.* **435**, 194, Note 1 (1924). (9) de Graef, *Bull. soc. chim. Belg.* **34**, 428–429 (1925).

3:4330 2-CHLORONAPHTHOIC ACID-1  $C_{11}H_7O_2Cl$ Beil. IX-651
IX₁—

M.P. 152–153° (1)
151–152° (2)
151° (4)

Cryst. from C_6H_6 (2). — Sol. in 1000 pts. aq. at 20° or in 126 pts. aq at 100°; eas. sol. alc., ether (1).

[For prepn of C̄ from 2-hydroxynaphthoic acid-1 [Beil. X-328, X_1-(144)] with PCl_5 (3 moles) in s.t. at 180–190° for 8 hrs. followed by treatment with aq. see (1) (2); from 1-chloroformylnaphthyl-2-phosphoric acid dichloride [Beil. X-329] with PCl_5 (2 moles) in s.t. at 180–190° followed by treatment with aq see (1) (2); from 2-chloro-1-(chloromethyl)-naphthalene (4) by oxidn. with dil HNO_3 for 15 days see (4).]

C̄ in aq. susp. with 2% Na/Hg yields (1) α-naphthoic acid (1:0785), m.p. 160° (1).

C̄ does not esterify upon treatment in MeOH with HCl gas (3).

Salts: $CaĀ_2.2H_2O$; sol. in 150 pts. cold aq or 75 pts. hot aq.; loses water of hydration completely at 180° (1).

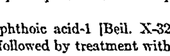
Ⓓ Methyl 2-chloro-1-naphthoate: pr. from alc. + toluene, m.p. 50° (1) (2), b.p. 176–180° at 18.5 mm. (2). [From AgĀ with MeI in s.t at 100° (1) or from C̄ with ethereal diazomethane (2).] [This ester is very resistant to hydrolysis (1) (2).]

—— Ethyl 2-chloro-1-naphthoate: unreported.

—— *p*-Bromophenacyl 2-chloro-1-naphthoate: unreported.

3:4330 (1) Rabe, *Ber.* **22**, 394–396 (1889). (2) Bergmann, Hirshberg, *J. Chem. Soc.* **1936**, 333–334. (3) Meyer, *Ber.* **28**, 184 (1895). (4) Horn, Warren, *J. Chem. Soc.* **1946**, 144.

3:4335 2,4,5-TRICHLOROPHENOXYACETIC ACID $C_8H_5O_3Cl_3$ Beil. S.N. 522



M.P. 153° (1)

Colorless cryst. from C_6H_6; alm insol. aq. — Neut. Eq. = 255.5.

[For prepn of C̄ from 2,4,5-trichlorophenol (3:1620) with chloroacetic acid (3:1370) in aq. NaOH (85% yield) see (1).]

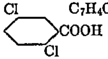
[For use of C̄ as weed killer see (2); for general survey of activity of C̄ as plant hormone see (4) (5).]

[For prepn. of ethylene glycol *bis*-(2,4,5-trichlorophenoxyacetate), m.p. 140°, and its use as plasticizer see (3).]

3:4335 (1) Pokorny, *J. Am. Chem. Soc.* **63**, 1768 (1941). (2) Hamner, Tukey, *Science* **100**, [illegible]

[illegible] (1944), C.A. **39**, 4315 (1945).

3:4340 **2,5-DICHLOROBENZOIC ACID**



$C_7H_4O_2Cl_2$ Beil. IX - 342 IX_1-(141)

M.P. 155°	(1)	153°	(7) (8)	B.P. 301° (12)
154.5°	(2)	152°	(9)	
154.4°	(3)	151–152°	(10)	
154°	(4) (21)	150°	(11)	
153.5°	(5)	149–150°	(12)	
153.0–153.5°	(6)	147–148°	(13)	

Ndls. from aq. or dil. alc. — Somewhat volatile with steam. — Sol. in 1193 pts. aq. at 11° (12); in 1177 pts. at 14° (11).

[For prepn. of $\bar{C}$ from 2,5-dichlorotoluene (3:6245) by htg. with dil. HNO_3 in s.t. at 140° (60% yield (4)) (5) (13) (2) (8) (7) or htg. with $KMnO_4$ (14) see indicated refs.; for prepn. of $\bar{C}$ from 2,5-dichlorobenzaldehyde (3:1145) via Cannizzaro reactn. (84% yield (1)) see (1) (4); for prepn. (90–95% yield (9)) from 5-chloro-2-aminobenzoic acid via diazo reactn + CuCl see (9) (11); from 2,5-dichloroaniline via 2,5-dichlorobenzonitrile (m.p. 130°) and its hydrolysis with fumg. HCl at 180° see (15); for prepn. of $\bar{C}$ from benzoic acid + $KClO_3$ + HCl see (12) (21); for still other misc. methods see Beil. IX-342, IX_1-(141).]

For f.p./compn. data on mixtures of $\bar{C}$ with *m*-chlorobenzoic acid, m.p. 154.4° (3:4392), and with 2,3-dichlorobenzoic acid, m.p. 154.4° (3:4650), see (2).

$\bar{C}$ on htg. with 3 pts. conc. H_2SO_4 + 2 pts. aq. loses CO_2 at 220° yielding *p*-dichlorobenzene (3:0980) (5).

The direct nitration of $\bar{C}$ is unrecorded. [However, 2,5-dichloro-3-nitrobenzoic acid, ndls. from AcOH, m.p. 220°, and 2,5-dichloro-6-nitrobenzoic acid [Beil. IX-404], m p. 143–144°, have both been prepd. by oxidn. (16) of the corresp. aldehydes.]

$\bar{C}$ with PCl_5 (17) or with $SOCl_2$ (18) yields 2,5-dichlorobenzoyl chloride, b.p. 137° at 15 mm. (17), 95 3–95.5° at 1 mm. (18). [For formn. in chlorination of benzoyl chloride see (2)]

—— **Methyl 2,5-dichlorobenzoate:** unrecorded.

—— **Ethyl 2,5-dichlorobenzoate:** b.p. 271° cor. (12). [For study of hydrolysis see (20).]

Ⓓ **2,5-Dichlorobenzamide:** woolly ndls. from aq., m.p. 155° (12).

Ⓓ **2,5-Dichlorobenzanilide:** from 2,5-dichlorobenzoyl chloride (above) + aniline (11), pr. from C_6H_6, m.p. 240° (11).

Ⓓ **2,5-Dichlorobenz-3-nitroanilide:** from 2,5-dichlorobenzoyl chloride (above) + *m*-nitroaniline (19), ndls from aq. MeOH, m.p. 151–152° u.c. (19).

3:4340 (1) Lock, *Ber.* **66**, 1531 (1933). (2) Hope, Riley, *J. Chem. Soc.* **123**, 2470–2480 (1923). (3) Bornwater, Holleman, *Rec. trav chim.* **31**, 227–230 (1912). (4) de Crauw, *Rec. trav. chim.* **50**, 773 (1931). (5) Lellmann, Klotz, *Ann.* **231**, 319 (1885). (6) Gassmann, Hartmann, *J. Am. Chem. Soc.* **63**, 2394 (1941). (7) Cohen, Dakin, *J. Chem. Soc.* **79**, 1130 (1901). (8) Turner, Wynne, *J. Chem. Soc.* **1936**, 712. (9) Eller, Klemm, *Ber.* **55**, 222 (1922). (10) Twiss, Farinholt, *J. Am. Chem. Soc.* **58**, 1564 (1936).

(11) Hübner, *Ann.* **222**, 201–203 (1883). (12) Beilstein, *Ann.* **179**, 290–293 (1875). (13) Feldmann, Kopeliowitsch, *Arch. Pharm.* **273**, 491 (1935). (14) Ullmann, Wagner, *Ann.* **371**, [illegible] 356. (20) Blakey, McCombie, Scarborough, *J. Chem. Soc.* **1926**, 2863–2868. (21) Biswas, Das-Gupta, *J. Indian. Chem. Soc.* **19**, 497–498 (1942); *C.A.* **37**, 5709 (1943).

3:4355 2-CHLORO-4-METHYLBENZOIC ACID  $C_8H_7O_2Cl$ Beil. IX - 497 IX_1—

M.P. 155.0–155.5° u.c. (1)
149–150° (2)

Colorless ndls. from alc.; spar. sol. cold, more sol hot, aq.; eas. sol. alc., ether, $CHCl_3$, hot C_6H_6.

[For prepn. of C̄ from 3-chloro-4-isopropyl-1-methylbenzene (3-chloro-*p*-cymene) (3.8770) by oxidn. with 15 pts. boilg. HNO_3 (D = 1.24–1.29) (other products are also formed) see (2), from 3-chloro-4-methylbenzonitrile, m.p. 61–62° (1), by hydrol. with boilg aq KOH (100% yield) see (1).]

Salts. $NH_4\bar{A}$, $K\bar{A}$, $Na\bar{A}.H_2O$, all very eas. sol. both in aq. and in alc. (1); $Ca\bar{A}_2.2H_2O$, $Ba\bar{A}_2$ $5H_2O$, eas. sol. hot aq. (1), $Ag\bar{A}$, spar. sol. cold aq. but eas. sol. hot aq. (1).

[C̄ on mononitration by soln. in fumg. HNO_3 (D = 1.5) at ord. temp. followed by stdg. several hrs. ppts. 2-chloro-5-nitro-4-methylbenzoic acid [Beil. IX-503], cryst. from hot aq or alc., m.p 180° u.c. (1), 180–181.5° u c (3), 180–181° (4) (note that the isomeric 2-chloro-3-nitro-4-methylbenzoic acid [Beil. IX-503], m.p. 192° u.c. (3), may be formed from C̄ under certain conditions (3)).]

[C̄ on dinitration with mixt. of 1 pt. fumg. HNO_3 (D = 1.52) + 4 pts. conc. H_2SO_4 gives (3) either in cold or on htg. exclusively 2-chloro-3,5-dinitro-4-methylbenzoic acid [Beil. IX-506], ndls. from alc., m.p. 233° u.c. (3).]

—— **Ethyl 2-chloro-4-methylbenzoate:** oil, b.p. not reported; $D_4^{21.4}$ = 1.1591 (5), $n_{He}^{21.4}$ = 1.52443 (5)

—— **2-Chloro-4-methylbenzamide:** ndls. from alc., m.p. 182° (1) [From partial alk. hydrolysis of 2-chloro-4-methylbenzonitrile (see above) (1).]

3:4355 (1) Claus, Davidsen, *J. prakt. Chem.* (2) **39**, 491–496 (1889). (2) Fileti, Crosa, *Gazz. chim ital* **16**, 288–290 (1886). (3) Claus, Davidsen, *Ann* **265**, 345–346, 348–349 (1891). (4) Fileti, Crosa, *Gazz. chim ital.* **18**, 312 (1888). (5) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 18 (1929)

3:4375 *p*-CHLOROPHENOXYACETIC ACID $C_8H_7O_3Cl$ Beil. VI - 187 VI_1— VI_2-(177)

M.P. 156.7–157.2° cor. (6)
155–156° (1) (4) (5)
151° (2) (3)

Pr. (from hot aq.). — Spar sol. cold aq.

[For prepn from *p*-chlorophenol (3:0475) by htg. with chloroacetic ac. (3:1370) and aq. alk. see (1) (4) (5) (6).]

C̄ htd. with conc. HCl in s t. at 150° yields *p*-chlorophenol (3:0475) (3)

C̄ refluxed with 1½ pts. thionyl chloride for 1½ hrs. gives (90% yield) *p*-chlorophenoxyacetyl chloride, b.p. 142° at 17 mm, m p. 18.8° (1).

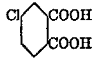
The methyl ester (b p. 177–180°) and the ethyl ester, ndls. (from alc.), m p. 49°, have been prepared from the acid chloride (1)

***p*-Chlorophenoxyacetamide:** from the acid chloride by treatment with excess $(NH_4)_2CO_3$; ndls. from alc., m.p. 133° (1).

p-Chlorophenoxyacetanilide: from the acid chloride by action of aniline (2 moles) in C_6H_6; ndls. (from alc.), m.p. 125° (1).

3:4375 (1) Minton, Stephen, *J. Chem. Soc.* **121**, 1599–1601 (1922). (2) Michael, *Am. Chem. J.* **9**, 216 (1887). (3) Peratoner, *Gazz. chim. ital.* **28**, I 239 (1898). (4) Behaghel, *J. prakt. Chem.* **114**, 297–298 (1926). (5) Koelsch, *J. Am. Chem. Soc.* **53**, 304–305 (1931). (6) Hayes, Branch, *J. Am. Chem. Soc.* **65**, 1555–1564 (1943).

3:4390 4-CHLOROPHTHALIC ACID



$C_8H_5O_4Cl$ Beil. IX - 816
IX_1-(366)

M.P. **157°** (1)
156° (2)
151° (3)
150–150.5° (4)
150° in s.t. (5)
148° u.c. (6)

[*See also 4-chlorophthalic anhydride* (3:2725).]

Ndls. from alc.; cryst. from C_6H_6 or CCl_4. — Eas. sol. aq., alc., ether, or AcOH.

[For prepn. of $\bar{C}$ from 4-chlorophthalic anhydride (3:2725) by warming with aq. or from dimethyl 4-chlorophthalate (3) or diethyl 4-chlorophthalate (5) by hydrol. with alk. see indic. refs.; from neutral sodium phthalate in aq. alk. on treatment with Cl_2 see (3) (7) (8) (9) (10); from 4-chloro-2-methylbenzoic acid (3:4700) (11) (12), from 5-chloro-2-methylbenzoic acid (3:4670) (11), from 4-chloro-2-methylacetophenone [Beil. VII-306] (2), or from 7-chloro-1,2,3,4-tetrahydronaphthalene (1) by oxidn. with alk. $KMnO_4$ see indic. refs.; from 6-chloroindanone-1 [Beil. VII-361] on evapn. with hot 25% HNO_3 see (4); from 1,6-dichloronaphthalene (3:0810) (13), 2,6-dichloronaphthalene (3:4040) (14) (6), 2,7-dichloronaphthalene (3:3445) (14), 6-chloronaphthol-2 (3:3500) (6), or 4-chloro-2-methylbenzoic acid (above) (12) on oxidn. with dil. HNO_3 in s t. as directed see indic. refs.; from the trichloride of 4-sulfophthalic acid [Beil. XI-407] with PCl_5 in s.t. at 220° followed by KOH hydrolysis of the 4-chlorophthalyl (di)chloride see (15); from 4-sulfophthalic anhydride (16) by htg. with HCl + $NaClO_3$ see (16).]

$\bar{C}$ on htg. above m.p. gives 4-chlorophthalic anhydride (3:2725).

[$\bar{C}$ on fusion with KOH (11) or with NaOH at 165–175° (10) gives (100% yield (10)) 4-hydroxyphthalic acid [Beil. X-499, X_1-(255)], m.p. 204–205°, with conv. to corresp. anhydride, m p. 171° (note that this same prod. is also obtd. from the isomeric 3-chlorophthalic acid (3:4820)).]

[$\bar{C}$ htd. under press. at 350° with aq. + cat. loses CO_2 presumably yielding (17) *m*-chlorobenzoic acid (3:4392) and/or *p*-chlorobenzoic acid (3:4940).]

[$\bar{C}$ with NH_3 gas + cat. as directed (18) yields 4-chlorophthalonitrile, m.p. 130–132° (19).]

[For use of $\bar{C}$ as softener for cellulose derivatives see (20); for reaction of $\bar{C}$ with naphthalene + $AlCl_3$ yielding intermediates for vat dyes see (21).]

$\bar{C}$ on htg. with resorcinol + few drops conc. H_2SO_4, then dissolving in alk., gives fluorescein reactn. (2). — $\bar{C}$ is unstable toward $KMnO_4$ (2).

Salts. *Ba$\bar{A}$, Ca$\bar{A}$, dif. sol. aq.; Ba$\bar{A}$.$H_2\bar{A}$, spar. sol. even in hot aq. (11) (for table of* heavy metal salts see (22)).

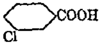
Esters. Dimethyl 4-chlorophthalate; from $Ag_2\bar{A}$ with MeI (15), from 4-chlorophthalyl (di)chloride (above) with MeOH (15), or from $\bar{C}$ in MeOH with HCl gas (3); ndls. from

lgr., m.p. 38° (3), 37° (15), b.p. 186–187° at 32 mm. (3); diethyl 4-chlorophthalate; from C̄ in alc. with HCl gas (15) or from diethyl 4-aminophthalate via diazotization and use of Cu_2Cl_2 reactn. (70% yield (5)), b.p. 300–305° (15), 185–190° at 25 mm. (5), 173–174° at 16 mm. (1).

3:4390 (1) von Braun, Larbig, Kredel, *Ber.* **56**, 2337–2338 (1923). (2) Mayer, Albert, Schön, *Ber.* **65**, 1297 (1932). (3) Ayling, *J. Chem Soc.* **1929**, 253–256. (4) Miersch, *Ber.* **25**, 2116 (1892). (5) Blicke, Smith, *J. Am. Chem. Soc.* **51**, 1869 (1929). (6) Claus, Dehne, *Ber.* **15**, 320–321 (1882). (7) Moore, Marrack, Proud, *J. Chem. Soc.* **119**, 1788–1789 (1921). (8) Egerer, Meyer, *Monatsh.* **34**, 81–83 (1913). (9) Scottish Dyes, Ltd., Beckett, Bangham, Thomas, Brit. 348,632, June 11, 1931; *Cent.* **1931**, II 1194 (10) Rushchinskiĭ, *Compt. rend acad. sci.* (*U.R.S.S.*) **1933**, 118–121; *Cent* **1935**, I 1617.

(11) Krüger, *Ber.* **18**, 1758–1759 (1885). (12) Claus, Stapelberg, *Ann.* **274**, 289 (1893). (113) Cleve, *Bull. soc. chim.* (2) **29**, 499 (1878). (14) Alén, *Bull soc. chim.* (2) **36**, 433–434 (1881). (15) Rée, *Ann.* **233**, 237–238 (1886). (16) Waldmann, Schwenk, *Ann.* **487**, 290–291 (1931). (17) Jaeger (to Selden Co), U.S. 1,953,231, Apr. 3, 1934; *Cent.* **1934**, II 1688. (18) Imperial Chem. Ind., Ltd. French 766,944, July 6, 1934; *Cent.* **1934**, II 2749 (19) Soc. Chem. Ind. Basel, French 844,567, July 27, 1939, *C.A.* **34**, 7299 (1940). (20) Dreyfus, French 749,792, July 29, 1933; *Cent.* **1934**, I 3154.

(21) B.A.S.F., French 599,038, Dec. 31, 1925; *Cent.* **1926**, I 2850. (22) Ephraim, *Ber.* **55**, 3482 (1922).

3:4392 *m*-CHLOROBENZOIC ACID  $C_7H_5O_2Cl$ Beil. IX - 337 IX_1-(139)

M.P.	159°	(105)	154.5°	(11) (12)
	158°	(1) (2) (3)	154.4°	(13)
	157.5°	(3) (4)	154.25°	(14)
	157°	(5)	154–155°	(15)
	156.2°	(6)	154°	(16) (17) (18) (60)
	155–156° cor.	(7)	153–154°	(24)
	156°	(26)	153.5°	(19)
	155°	(8)	153°	(20) (21) (26) (28) (35)
	154.8–155.0° cor.	(62)		(70) (84)
	154.9°	(8)	152°	(22) (47)
	154.8–154.9°	(9)		
	154.8°	(10)		

Pr. from hot aq., 30% AcOH or C_6H_6. — C̄ is spar. sol. cold aq., e g., 1 pt. C̄ is sol. at 0° in 2840 pts. aq (23); 100 ml. satd. aq. soln. at 25° conts. 0.0385 g. C̄ (60). — C̄ is eas. sol. hot aq, alc., ether. — At 14–16° C 100 ml. of satd. soln. of C̄ in ether conts. 14 g. C̄; in C_6H_6, 0 66 g. C̄; in CS_2, 0 62 g. C̄; in CCl_4, 0.08 g. C̄ (8). — For study of soly. of C̄ in C_6H_6 or *n*-heptane see (11); in chlorobenzene (3:7903), in *o*-chlorotoluene (3:8245), or in *m*-chlorotoluene (3:8275) see (10); in acetone or C_6H_6 see (6); for soly. of C̄ in aq. solns. of various salts including NaĀ see (60). — For distribution coefficients of C̄ at 25° between aq. + toluene or between aq. and $CHCl_3$ see (102).

C̄ can be sublimed under reduced press. (24) (14). — C̄ is but very slightly volatile with steam (for details see (12)). — For study of adsorption of C̄ by charcoal from acetone or C_6H_6 soln. see (6).

Binary systems contg. C̄: [For f.p./compn. data on system C̄ + H_2O see (25). — For f.p./compn data and diagram of system C̄ + benzoic acid (1:0715) (eutectic, m.p. 96 0° (20), 95.4° (27) (8), contg. 36 wt. % C̄ (27) (20) (8) (28)) see indic. refs. — For f.p./compn. data on systems C̄ + *m*-toluic acid (1:0705) (26), C̄ + *m*-hydroxybenzoic acid (1:0825) (26), see indic. refs.]

[For f.p./compn. data on system $\bar{C}$ + *o*-chlorobenzoic acid (3:4150) (eutectic, m.p. 110.7°, contg. 47–48 mole % $\bar{C}$ (20) (27) (8) (19)) see indic. refs.; on system $\bar{C}$ + *p*-chlorobenzoic acid (3:3940) (eutectic, m.p. 140.9°, contg. 80 mole % $\bar{C}$ (8) (19) cf. (104)) see indic. refs.; on system $\bar{C}$ + 2,5-dichlorobenzoic acid (3:4340) (eutectic, m.p. 119.7°, contg. 51–58 mole % $\bar{C}$) see (13).]

[For f.p./compn. data on systems $\bar{C}$ + *o*-bromobenzoic acid (28), $\bar{C}$ + *m*-bromobenzoic acid (28), $\bar{C}$ + *p*-bromobenzoic acid (28), *m*-iodobenzoic acid (29), *o*-nitrobenzoic acid (30), *m*-nitrobenzoic acid (30) see indic. refs.]

Ternary systems contg. $\bar{C}$: [For influence of addn. of benzoic acid (20) or of *p*-chlorobenzoic acid (3:4940) (27) to eutectic of $\bar{C}$ with *o*-chlorobenzoic acid (3:4150) see indic. refs. — For influence of addn. of *o*-chlorobenzoic acid (3:4150) to eutectic of $\bar{C}$ with benzoic acid (1:0715) see (27); for data on system $\bar{C}$ + *o*-chlorobenzoic acid (3:4150) + *p*-chlorobenzoic acid (3:4940) see (19).]

Miscellaneous. [For study of fate of $\bar{C}$ in animal organism see (31) cf. (102) (note that although from man $\bar{C}$ is excreted (34) as *N*-(*m*-chlorobenzoyl)glycine (*m*-chlorohippuric acid) [Beil. IX-339], m.p. 143–144° (31), yet from dog and rabbit no evidence for this conjugation product has been found (31). — For study of use of $\bar{C}$ as a preservative see (32). — For use of $\bar{C}$ as vulcanization regulator see (33).]

Preparation. [For prepn. of $\bar{C}$ from benzoic acid (1:0715) by chlorination with Cl_2 (38) in pres. of $FeCl_3$ (70% yield (8)), with $KClO_3$ + conc. HCl (35) (36) (37) (38), with aqua regia at 100° (yield 32% (39)) (7), with $SbCl_5$ (35) (40) (84), with MnO_2 + conc. HCl in s.t. at 150° (41), with NaOCl soln. (20) (42), or with $Ca(OCl)_2$ soln. (42) (35) (38) see indic. refs. (note that in all these cases numerous other chlorination products are also formed); from cinnamic acid (1:0735) by chlorination and oxidn. with $Ca(OCl)_2$ soln. see (35) (38).]

[For prepn. of $\bar{C}$ by oxidn. of *m*-chlorotoluene (3:8275) with $K_2Cr_2O_7$ + H_2SO_4 (43), with 5% aq. $KMnO_4$ (75% yield (4)) (8), with dil. HNO_3 in s.t. at 130–140° for 8 hrs. (47), or in aq. alk. at 260° under press. with air (44) see indic. refs.; from 3-chlorobiphenyl (3:8940) or from 3,3′-dichlorobiphenyl (3:0180) by oxidn. with CrO_3/AcOH in pres. of V_2O_5 see (45); from *m*-chlorobenzaldehyde (3:6475) by oxidn. with alk. $KMnO_4$ see (3).]

[For prepn. of $\bar{C}$ from *m*-chlorobenzal (di)chloride (3:6710) by hydrolysis with aq followed by $KMnO_4$ oxidn. (7% yield (2)) or from its mixt. with *m*-chlorobenzotrichloride (3:6845) by hydrolysis with 70% H_2SO_4 or 80% AcOH or 5% NaOH at 90–100° in stream of air to effect immediate oxidn. (46) see indic. refs.]

[For prepn. of $\bar{C}$ from *m*-chlorobenzonitrile [Beil. IX-339], m.p. 40.5° (48), by hydrolysis with conc. H_2SO_4 (3), from *N*-(*m*-chlorobenzoyl)glycine (*m*-chlorohippuric acid) by hydrolysis with HCl (35) (36), see indic. refs.]

[For prepn. of $\bar{C}$ from *m*-aminobenzoic acid [Beil. XIV-383, XIV_1-(558)] via dizaotization and use of Cu_2Cl_2 reactn. (74% yield (101)) (3) (4) (49); from *m*,*m*′-diazoaminobenzoic acid (diazoaminobenzene-3,3′-dicarboxylic acid) [Beil. XVI-727] with warm conc. HCl (50) see indic. refs.]

[For formn. of $\bar{C}$ from *m*-chloro-iodobenzene [Beil. V-220, V_2-(167)] by reaction with *n*-butyllithium in ether followed by carbonation with CO_2 (41.5% yield (51)); from *p*-chloronitrobenzene [Beil. V-243, V_1-(129), V_2-(182)] with alc. KCN in s t. at 200° (52); from 3-chlorophthalic acid (3:4820) or 4-chlorophthalic acid (3:4390) by cat. partial decarboxylation (53); from 3-chlorophthalic acid by mercuration and treatment with HCl (99) see indic. refs.]

Chemical behavior. [$\bar{C}$ (as Na$\bar{A}$) on reduction in boilg. aq. soln. with Na/Hg yields (36) (54) benzoic acid (1:0715) (for study of reduction of $\bar{C}$ with H_2 + Ni in aq. alk. at ord. temp. see (55)); $\bar{C}$ on *electrolytic reduction in alc./H_2SO_4 yields* (56) *m*-chlorobenzyl

alcohol [Beil. VI-444], oil, b.p. 234° (56); note that $\bar{C}$ with Ni/Al alloy (Raney nickel) in aq. alk. soln. at 90° gives (100% yield (106)) benzoic acid (1:0715), m.p. 121°.]

$\bar{C}$ behaves normally as a monobasic acid: e g., $\bar{C}$ on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization const. at 25° is 1.55×10^{-4} (57), $1.53–1.59 \times 10^{-4}$ (58), 1.506×10^{-4} (59) cf. (1) (60). — [For study of acid strength of $\bar{C}$ in MeOH, EtOH, and various other alcs. see (61) (62) (63) (16) (64) (65) (17).]

Salts of inorganic bases. [$NH_4\bar{A}$, m.p. 203–204° dec. (39), lfts. from acetone/pet. ether (39), powder from abs alc (66). — Hydroxylamine salt, ndls. from xylene, m.p. 144° (72), 145–146° dec. (39). — $Na\bar{A}$ (67), $K\bar{A}$ (67) both behave as liquid cryst. on fusion. — $Ag\bar{A}$, insol. aq. (68) (note that this salt (1 mole) with I_2 (2 equiv.) in dry C_6H_6 refluxed 15–18 hrs. yields (69) phenyl *m*-chlorobenzoate, m.p. 53°, + CO_2 + AgI). — $Ca\bar{A}_2.3H_2O$, sol. at 12° in 82 6 pts. aq. (68) (35). — $Ba\bar{A}_2.4H_2O$, eas. sol. aq. or alc. (for use in sepn. of $\bar{C}$ from *o*-chlorobenzoic acid (3:4150) and *p*-chlorobenzoic acid (3:4940) see (27)). — $Cd\bar{A}_2.2H_2O$ (71).]

Salts of organic bases. E.g., $\bar{C}$ with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (73) benzylammonium·*m*-chlorobenzoate, m.p. 146.8–147.4° u c., 149 2–149 8° cor. (73), Neut. Eq. 263.6 (note that the m.p. of this salt is only very slightly lower than that of the corresp. salt from *o*-chlorobenzoic acid (3:4150)). — $\bar{C}$ similarly treated with α-phenylethylamine yields (73) α-phenylethylammonium *m*-chlorobenzoate, m.p 142 0–142 6° u c., 144 7–145.3° cor. (73), Neut. Eq 277.6 (note that the m.p. of this salt, although better separated from those of the isomeric acids than the preceding case, is very close to that for the corresp. deriv. of cinnamic acid (1:0735)).

$\bar{C}$ (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, in alc htd. several minutes, solvent evaporated, and resulting syrup recrystallized from aq. yields (74) codeine *m*-chlorobenzoate, $C_{18}H_{21}O_3N.\bar{C}$, m.p 96° on "Maquenne block"; note that this m.p. although very close to that (99°) of corresp. salt from *m*-bromobenzoic acid is widely different from the corresp. salts of *o*-chlorobenzoic acid (3:4150) and *p*-chlorobenzoic acid (3:4940), which are 134° and 162° respectively. — $\bar{C}$ (1 mole) in alc. (or $CHCl_3$) with strychnine (1 mole) in alc. boiled for a few minutes then cooled yields (75) strychnine *m*-chlorobenzoate, $C_{21}H_{22}O_2N_2.\bar{C}$, m.p 185° u c. on "Maquenne block"; note that this m.p. is somewhat higher than that (170°) of the corresp. salt from *o*-chlorobenzoic acid (3:4150) and widely different from that (251°) of the corresp. salt of *p*-chlorobenzoic acid (3:4940).

$\bar{C}$ with alcohols gives by conventional procedures the corresp. esters; for details on methyl *m*-chlorobenzoate (3:6670) and on ethyl *m*-chlorobenzoate (3:6770) see these compds. — [For study of rate of esterification of $\bar{C}$ with MeOH (76) or with cyclohexanol (77) see indic. refs.]

$\bar{C}$ with P_2O_5 in toluene boiled for 4 hrs. (78) or $\bar{C}$ with oxalyl (di)chloride (3:5060) refluxed in C_6H_6 (79) cf. (80) yields *m*-chlorobenzoic acid anhydride, pl. from C_6H_6 or toluene, ndls. from lt. pet. or alc , m p. 95.5° (78), 95° (79) (note that $\bar{C}$ (2 moles) with oxalyl (di)bromide refluxed in C_6H_6 similarly gives good yields (80) of the above anhydride but $Na\bar{A}$ with oxalyl dibromide can also be used (80) to prepare *m*-chlorobenzoyl bromide, oil, b p. 143–147° at 40 mm. (80)).

$\bar{C}$ with PCl_5 (31) (68) (3) or with $SOCl_2$ (81) (82) or with $SOCl_2$ + pyridine (83) gives (76% yield (31)) *m*-chlorobenzoyl chloride (3:6590), b p. 225°.

[$\bar{C}$ with HN_3 in conc. H_2SO_4 in trichloroethylene (3:5170) soln. at 40° gives (75% yield (107)) *m*-chloroaniline]

$\bar{C}$ fused with KOH, subsequently acidified, yields (84) *m*-hydroxybenzoic acid (1:0825).

$\bar{C}$ on nitration with boilg. fumg. HNO_3 for 10 min. (70) or with abs. HNO_3 at 0° or −30° (3) (21) (85) gives a mixt. of two isomeric nitro-*m*-chlorobenzoic acids; this mixt. consists mainly (92–93% (86) cf. (21)) of 3-chloro-6-nitrobenzoic acid [Beil. IX-401],

cryst. from HNO_3 (D = 1.1) (24), ether, C_6H_6, or aq., m.p. 139° (85), 137–138° (70), 136° (3), 135–136° (24), accompanied by a little (7–8% (86)) cf. (24) 3-chloro-2-nitrobenzoic acid [Beil. IX-400], ndls. or tbls. from hot aq., m.p. 235° (70) (85), 233–234° (3) (for details on sepn. of these two isomers see (3) (70) (24) (85)). — Note that the other two possible nitro-m-chlorobenzoic acids are known but are not found in the product from nitration of C̄; they are 3-chloro-4-nitrobenzoic acid [Beil IX-404], m.p. 185–186°, and 3-chloro-5-nitrobenzoic acid [Beil. IX-403, IX_1-(165)], m.p. 147°. — [Note also that *no* dinitro-3-chlorobenzoic acids have ever been reported.]

—— **Methyl m-chlorobenzoate:** b.p. 231°, m.p. 21°. (See 3:6670.)

—— **Ethyl m-chlorobenzoate:** b.p. 245°. (See 3:6770.)

Ⓓ **p-Nitrobenzyl m-chlorobenzoate:** m.p. 107.2° u.c. (87). [From C̄ (as NaĀ) with p-nitrobenzyl bromide (m.p. 99°) in boilg. dil. alc. (87); note that m.p. of this ester is almost identical with that (106° (88)) of the corresp. ester of o-chlorobenzoic acid (3:4150).]

Ⓓ **Phenacyl m-chlorobenzoate:** m.p. 118° (89), 116.4° (21). [From C̄ (as NaĀ) with phenacyl bromide (m.p. 50°) in boilg. alc. (98% yield (21)).]

—— **p-Chlorophenacyl m-chlorobenzoate:** unreported.

Ⓓ **p-Bromophenacyl m-chlorobenzoate:** m.p. 117.2° (21), 116° (90). [From C̄ (as NaĀ) with p-bromophenacyl bromide (m.p. 109°) in boilg. alc. (21).]

—— **p-Iodophenacyl m-chlorobenzoate:** unreported.

Ⓓ **p-Phenylphenacyl m-chlorobenzoate:** m.p. 154° u.c. (91). [From C̄ (as NaĀ) with p-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (91); note that the m.p. of this deriv. is only slightly lower than that (160° u c. (91)) of the corresp. ester of p-chlorobenzoic acid (3:4940); note also that, since this ester has almost the same m.p. as the original C̄, care must be taken to show that the supposed ester is insol. in aq. Na_2CO_3 (dif. and sepn. from C̄); note finally that the m.p. of a mixt. of C̄ with this ester is depressed to 130–132° (91).]

Ⓓ **S-Benzylthiuronium m-chlorobenzoate:** cryst. from alc., m.p. 155° cor. (92). [From NaĀ or KĀ in dil. alc. with slight excess S-benzylthiuronium chloride soln. (15% in hot alc.) (92).]

Ⓓ **S-(p-Chlorobenzyl)thiuronium m-chlorobenzoate:** cryst from dioxane, m.p. 157° cor. (93). [From NaĀ or KĀ in aq. with 1 equiv. of S-(p-chlorobenzyl)thiuronium chloride, m.p. 197° (10% in alc.) (93); note that the m.p. of this prod. is closely adjacent to that (m.p. 159° cor. (93)) of the corresp. salt of o-chlorobenzoic acid (3:4150), and is also almost identical with that of the original C̄.]

Ⓓ **S-(p-Bromobenzyl)thiuronium m-chlorobenzoate:** m.p. 150° cor. (94). [From NaĀ or KĀ in aq. with 1 equiv. of S-(p-bromobenzyl)thiuronium bromide, m.p. 213°, in alc. (94).]

Ⓓ **m-Chlorobenzamide:** cryst. from hot aq. or alc., m p. 135° (100), 134 5° cor. (3), 134° u.c. (95), 132–133° (70). [From o-chlorobenzoyl chloride (3:6590) with conc. aq. NH_4OH (68) (70) or from C̄ by refluxing with AcOH + $(NH_4)_2CO_3$ (46–50% yield (100)); note that this amide gives on fusion with HgO a mercuric deriv., m.p. 245° u c. (95).]

Ⓓ **m-Chlorobenzhydrazide:** ndls. from aq. or alc , m.p. 158° (96), 157–158° (97). [From ethyl m-chlorobenzoate (3:6770) with hydrazine hydrate in abs. alc. on 8-hr. reflux. (yield: 97% (96), 87% (97)).] — [For use of m-chlorobenzhydrazide as general reagt. for identification of aldehydes and ketones see (97).]

—— **N'-(m-Chlorobenzoyl)-N-phenylhydrazide:** unreported.

—— *m*-Chlorobenzanilide: cryst. from alc., m.p. 122–125° (98). [Prepn. reported but only by indirect means (98).] — [Note that the isomeric benz-*m*-chloroanilide [Beil. XII-605] has m.p. 118°.]

—— *m*-Chlorobenzo-*p*-toluidide: unreported.

—— *m*-Chlorobenzo-α-naphthalide: unreported.

—— *m*-Chlorobenzo-β-naphthalide: unreported.

3:4392 (1) Dippy, Williams, Lewis, *J Chem. Soc* **1935**, 343–346. (2) Asinger, Lock, *Monatsh.* **62**, 335 (1933). (3) Montagne, *Rec. trav. chim* **19**, 51–59 (1900). (4) Koopal, *Rec. trav. chim.* **34**, 144 (1915). (5) Kailan, Antropp, *Monatsh.* **52**, 297, 307–310 (1929). (6) Berger, *Rec. trav* ... 1783. (8) ... rooks, Hol ... 30). (... *n. Soc.* **117**, 403–406 (1920). (13) Hope, Riley, *J. Chem. Soc* **123**, 2479 (1923). (14) Andrews, Lynn, Johnson, *J. Am. Chem. Soc* **48**, 1282 (1926). (15) Kellas, *Z. physik Chem.* **24**, 222, 230, 241, 245–246, 249, 251 (1897). (16) Wooten, Hammett, *J. Am. Chem. Soc.* **57**, 2291 (1933). (17) Kuhn, Wassermann, *Helv. Chim. Acta* **11**, 34 (1928). (18) Graebe, *Ann.* **138**, 200–202 (1866). (19) Johnston, Jones, *J. Phys. Chem.* **32**, 599–601 (1928). (20) Smith, *J. Chem. Soc.* **1934**, 213–218.

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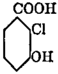
3:4395 2-CHLORO-3-HYDROXYBENZOIC ACID 

$C_7H_5O_3Cl$ **Beil. X - 142 X_1—**

M.P. 157.5–158.5° (1)
156.5–157.5° (1)
156–157° (2) (5)
156° (3)
155.0–155.5° u.c. (10)

Colorless lfts. from aq. or C_6H_6. [Ioniz. const. at 25° = 1.40×10^{-3} (5).]

[For prepn. of $\bar{C}$ from 2-chloro-3-hydroxybenzaldehyde (3:4085) with 5–6 pts. 50% KOH at 60–70° (Cannizzaro reactn.) (96% yield) see (3); from ethyl 2-chloro-3-hydroxybenzoate (see below) by hydrolysis with 35% KOH see (1) (2) cf. (4); for formn. from *m*-hydroxybenzoic acid (1:0825) with Cl_2 in MeOH (6) (44% yield (10)) or AcOH (1) (together with some of the isomeric 6-chloro-3-hydroxybenzoic acid (3:4720)) see indic. refs; for prepn. of $\bar{C}$ from 2-amino-3-hydroxybenzoic acid (1) via diazotization and use of Cu_2Cl_2 reactn. see (1).]

Salts: Ag$\bar{A}$, cryst. ppt. (2).

$\bar{C}$ in aq. soln. gives with $FeCl_3$ a violet-red color.

[$\bar{C}$ with formalin (1:0145) + conc. HCl + HCl gas at room temp. gives (87% yield (10)) 7-chloro-6-hydroxyphthalide, m.p. 290° cor. (10).]

—— **Methyl 2-chloro-3-hydroxybenzoate**: pr. with 1 H_2O from dil. alc., m.p. 70–71° (2); anhydrous form, m.p. 62–65° (2). [From $\bar{C}$ in MeOH with H_2SO_4 (2).] — [This ester with MeI + MeOH/KOH in s.t. at 130° for several hours gives methyl 2-chloro-3-methoxybenzoate, anhydrous ndls. from dil. alc., m.p. 41–42° (2).]

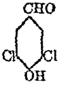
—— **Ethyl 2-chloro-3-hydroxybenzoate**: white ndls. with 1 H_2O from dil. alc., m.p. 58° (2); above m.p. loses aq. giving viscous oil (2). [From ethyl *m*-hydroxybenzoate (1:1471) with SO_2Cl_2 (together with the isomeric ethyl 6-chloro-3-hydroxybenzoate (2) (4)).] — [This anhydrous ester with AcCl yields ethyl 2-chloro-3-acetoxybenzoate, ndls. from dil. alc., m.p. 48–49° (2).]

—— **2-Chloro-3-methoxybenzoic acid**: colorless ndls. from aq., m.p. 161.5° (7), 160° (8) (9). [Prepd. indirectly from 2-chloro-3-methoxybenzaldehyde by oxidn. with $KMnO_4$ (7) (8).]

—— 2-Chloro-3-acetoxybenzoic acid: cryst. from aq. or C_6H_6, m.p. 152.5–153° u.c. (10). [From Č + Ac_2O + K_2CO_3 (10)]

3:4395 (1) Beyer, *Rec. trav. chim.* **40**, 626–628 (1921). (2) Mazzara, *Gazz. chim ital.* **29**, I 380–383 (1899). (3) Lock, *Monatsh.* **55**, 310–311 (1930). (4) Mazzara, Bertozzi, *Gazz. chim. ital* **30**, II 87–88 (1900). (5) Coppadoro, *Gazz. chim. ital.* **32**, I 546 (1902). (6) Plazek, *Roczniki Chem.* **10**, 761–776 (1930), *Cent.* **1931**, I 1428; *C.A.* **25**, 1504 (1931). (7) Hodgson, Rosenberg, *J. Chem. Soc.* **1930**, 17 (8) Hodgson, Beard, *J. Chem. Soc.* **1926**, 150. (9) Gibson, *J. Chem Soc.* **1926**, 1428. (10) Buehler, Harris, Shacklett, Block, *J. Am. Chem. Soc.* **108**, 577 (1946).

3:4400 3,5-DICHLORO-4-HYDROXYBENZALDEHYDE



$C_7H_4O_2Cl_2$ Beil. VIII - 81 VIII₁—

M.P. 158–159° cor. (1)
156° (2) (3)

Colorless odorless ndls. from dil alc or from $CHCl_3$, fairly eas. sol. alc., ether, AcOH; more dif. sol C_6H_6, lgr., $CHCl_3$

[For prepn. of Č from *p*-hydroxybenzaldehyde (1:0060) in 5 pts. AcOH at 100° (2) (4) or in $CHCl_3$ with cooling (1) with Cl_2 see indic refs.; from corresp. methyl ether (3,5-dichloro-4-methoxybenzaldehyde) with boilg. conc HI see (3)]

Č in *N* KOH with H_2O_2 yields (4) 2,6-dichlorohydroquinone (3:4600).

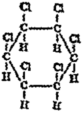
[The methyl ether of Č (see above) has been obtd. indirectly (3) from *p*-methoxybenzaldehyde (*p*-anisaldehyde) (1.0240) by chlorination with large excess (9 moles) SO_2Cl_2; bright red cryst from alc., m p 61 5° (3); on oxidn. with CrO_3 this prod. gives (80% yield (3)) 3,5-dichloro-*p*-methoxybenzoic acid [Beil. X-177], m p 202.0–202.5° (3)]

Ⓓ 3,5-Dichloro-4-hydroxybenzaldoxime: colorless ndls from dil. alc., m p. 185° (2). [From Č in moderately conc NaOH (3 moles) with $NH_2OH.HCl$ (1½ moles), subsequently acidified with AcOH (2).] — [This oxime on boilg. with Ac_2O for 2 hrs. yields (2) 3,5-dichloro-4-acetoxybenzonitrile, colorless cryst. from dil. alc., m.p. 93° (2).]

Ⓓ 3,5-Dichloro-4-hydroxybenzaldehyde semicarbazone: greenish yel. ndls. from AcOH, m.p. 236–237° cor. dec. (1) [From Č in hot AcOH (50 pts.) by addn. of conc aq. soln. of semicarbazide hydrochloride, followed by ½ hr. htg. (1)]

3:4400 (1) Biltz, *Ber* **37**, 4033–4034 (1904). (2) von Auwers, Reis, *Ber.* **29**, 2356–2358 (1896). (3) Durrans, *J. Chem. Soc.* **123**, 1426 (1923). (4) Dakin, *Am. Chem. J.* **42**, 490–491 (1909).

3:4410 *cis*-1,2,3,4,5,6-HEXACHLOROCYCLOHEXANE (α-Benzenehexachloride)



$C_6H_6Cl_6$ Beil. V - 23 V₁-(8) V₂-(11)

M.P. 158.2° (1)
158° (2)
157° cor. (3) (21)

[*See also β-benzenehexachloride* (3:4990).]

Nine stereoisomeric configurations of benzenehexachloride are possible (cf. (1)) and four are known; Č (contrary to earlier opinion (5)) is now thought (but not unequivocally proved) to have the *cis* configuration; the β-isomer has been shown to have the *trans* configuration; the configurations of the γ-isomer, m.p. 112–113° (2), and the δ-isomer, m p. 129–132° (2), are unknown.

C̄ cryst. from 80% AcOH (3) or from alc. — C̄ is volatile with steam (dif. and separation from β-isomer). — C̄ is insol. aq. but sol. in 22.8 pts. $CHCl_3$ at 15.25°; in 15 4 pts. C_6H_6 at 18 25° (5). — C̄ forms with the β-isomer a eutectic (m.p. 155.5°) contg. 79.7% C̄ (2).

[For manuf. of ordinary benzenehexachloride (mixt. of stereoisomers) from C_6H_6 (1:7400) + Cl_2 in pres. of light (6) (7) (8), X-radiation (9), or conc. H_2SO_4 (10) see indic. refs.; for study of prepn. of C̄ (together with other stereoisomers) from C_6H_6 with Cl_2 in pres. of 1% aq. *NaOH see (3) (2) (28), in gas phase (11) (12), in pres. of ethylene in the dark (13)*, in pres. of NCl_3 in the dark (14) or in light (15), in pres. of light (16) (17) (18) (19) (20).] [For use of C̄ as insecticide see (27); note, however, that insecticidal props. are thought to be due to γ-isomer (29).]

C̄ on htg. above its m.p. loses HCl and yields (3) (21) 1,2,4-trichlorobenzene (3:6420).

C̄ on htg. with aq in s.t. at 200° (19), on boilg. with MeOH/KOH (2), EtOH/KOH (2) (3) (19) (20) (22), alc. KCN (19), or pyridine (2), or on htg. with quinoline at 105–110° (2) yields mainly 1,2,4-trichlorobenzene (3:6420) together with other prods.; e.g, C̄ on boilg. with excess 10% alc KOH for ½ hr. (2) or C̄ boiled with 10 pts. pyridine for 1 hr. (2) gives (yield: 75–86% (2)) 1,2,4-trichlorobenzene (3:6420).

C̄ reacts very vigorously with boilg. aniline (19), but the prods. have not been detd.

[C̄ stood in s.t. with 3 pts. liq. Cl_2 for 11 days yields (23) α-nonachlorocyclohexane, cryst. *from alc, m.p. 95–96° (23) (24).]*

C̄ in alc. boiled with Zn dust yields (25) benzene (1:7400).

C̄ is very inert to most other reagents: e.g., C̄ can be recrystallized unchanged from fumg. HNO_3 (3), is unattacked by fumg H_2SO_4 (19), is unattacked by CrO_3 (3), is only slightly affected by aq. $KMnO_4$ even on boilg. (3), and is unaffected by conc. aq. NH_4OH (3), boilg. alc. $AgNO_3$ (3), or AgOAc (26).

3:4410 (1) van de Vloed, *Bull. soc. chim. Belg.* **48**, 255–256 (1938). (2) van der Linden, *Ber.* **45**, 231–247 (1912). (3) Matthews, *J. Chem. Soc.* **59**, 165–172 (1891). (4) Williams, Fogelberg, *J. Am. Chem. Soc.* **53**, 2103 (1931). (5) Friedel, *Bull. soc. chim.* (3) **5**, 130–138 (1891). (6) Hardie (to Imperial Chem. Ind., Ltd.), U.S. 2,218,148, Oct. 15, 1940; *C.A.* **35**, 1071 (1941). (7) Imperial Chem. Ind., Ltd., Grant, Brit. 504,569, April 26, 1939; *Cent.* **1939**, II 1775; *C.A.* **33**, 7822 (1939). (8) Stephenson, Curtis, Brit. 447,058, May 7, 1936; *Cent.* **1936**, II 3360; *C.A.* **30**, 6766 (1936). (9) Loiseau, French, 565,356, Jan. 25, 1924; *Cent.* **1925**, II 1227. (10) Battegay, French 641,102, July 28, 1928; *Cent.* **1928**, II 1718.

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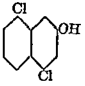
(21) Tei, Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.* **10-A**, 325–330 (1927); *Cent.* **1928**, I 2370; *C.A.* **22**, 1086 (1928). (22) Jungfleisch, *Ann. chim.* (4) **15**, 270 (1868). (23) van der Linden, *Rec. trav. chim.* **57**, 218–221 (1938). (24) Willgerodt, *J. prakt. Chem.* (2) **35**, 416 (1887). (25) Zinin, *Zeit. für Chemie* **1871**, 284. (26) Griffin, Nelson, *J. Am. Chem. Soc.* **37**, 1554 (1915). (27) Bender (to Great Western Electrochem. Co.), U.S. 2,010,841, Aug. 13, 1935; *Cent.* **1936**, I 1112. (28) Klingstedt, Wiese, Rüdback, *Acta Acad. Aboensis Math. et Phys.* **4**, No. 2, 1–36 (1927). (29) Taylor, *Nature* **155**, 393–394 (1945).

3:4420 *4,8-DICHLORONAPHTHOL-2*



$C_{10}H_6OCl_2$ Beil. VI — VI_1— VI_2-(604)

M.P. 158–159° (1).

Colorless ndls. from alc. — sol. in NaOH.

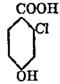
[For prepn. from 4,8-dichloronaphthylamine-2 via diazo reaction see (1).]

[For use in prepn. of azo dyestuffs see (2).]

C̄ on suitable methylation yields methyl ether, viz., methyl 2,4-dichloro-β-naphthyl ether, colorless ndls., m.p. 93° (1).

3:4420 (1) Friedländer, Karamessinis, Schenk, *Ber.* **55**, 48–49 (1922). (2) Herzberg, Wunderlich (to I.G.), Ger. 459,989, May 18, 1928; *Cent.* **1928**, II 395.

3:4430 2-CHLORO-4-HYDROXYBENZOIC ACID



$C_7H_5O_3Cl$ Beil. S.N. 1069

M.P. 159° (1)

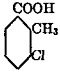
Colorless ndls. from aq.

[For prepn. of C̄ from 2-chloro-4-methoxybenzoic acid (see below) by cleavage with conc. HI (D = 1.7) see (1).]

[The corresp. methyl ether, viz., 2-chloro-4-methoxybenzoic acid (2-chloro-*p*-anisic acid), m.p. 208° (2) (3), has been obtd. indirectly from 2-chloro-4-methoxybenzaldehyde [Beil. VIII-81] (2) or from 2-chloro-4-methoxytoluene [Beil. VI-402] (3) by $KMnO_4$ oxidn. (2) (3).]

3:4430 (1) Hodgson, Jenkinson, *J. Chem. Soc.* **1927**, 1742. (2) Tiemann, *Ber.* **24**, 712 (1891). (3) Ullmann, Wagner, *Ann.* **355**, 368 (1907).

3:4435 3-CHLORO-2-METHYLBENZOIC ACID



$C_8H_7O_2Cl$ Beil. IX - 467
IX_1—

M.P. 159° (1)
156° (2)
154° (3)

Colorless ndls. from alc.; eas. sol. alc.

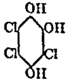
[For prepn. of C̄ from 3-chloro-2-methylbenzonitrile, m.p. 19° (1), by refluxing with 20% aq. KOH for 5 hrs. (98% yield) see (1); from 3-chloro-1,2-dimethylbenzene (3:8645) on oxdn. with boilg. dil. HNO_3 (D = 1.20) see (3); from 2-methylbenzoic acid (*o*-toluic acid) (1:0690) in $CHCl_3$ in pres. of Fe with Cl_2 (4) or in AcOH with Cl_2 (2) see indic. refs.]

Salts: $Ca\bar{A}_2.2H_2O$, spar. sol. hot aq. (3).

C̄ on oxdn. with $KMnO_4$ gives (3) 3-chlorophthalic acid (3:4820).

3:4435 (1) Noelting, *Ber.* **37**, 1025–1026 (1904). (2) Claus, Bayer, *Ann.* **274**, 310–311 (1893). (3) Krüger, *Ber.* **18**, 1758 (1885). (4) Claus, Stapelberg, *Ann.* **274**, 311 (1893).

3:4444 3,5,6-TRICHLORO-2-HYDROXYHYDROQUINONE



$C_6H_3O_3Cl_3$ Beil. VI - 1089
VI_1—
VI_2-(1072)

M.P. 160° (1)

Ndls. from C_6H_6 — C̄ cryst. from C_6H_6 or AcOH in solvated form. C̄ is eas. sol. alc., ether; spar. sol. pet. ether.

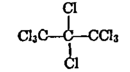
[For prepn. of $\bar{C}$ from 3,5,6-trichloro-2-hydroxybenzoquinone-1,4 [Beil. VIII-238] by reduction with aq. SO_2 see (1).]

$\bar{C}$ dis. in aq. yielding colorless soln. which on htg. develops violet color; $\bar{C}$ with aq. alk. gives deep green color changing to brown (1).

—— 3,5,6-Trichloro-2-hydroxyhydroquinone trimethyl ether: unreported.
—— 3,5,6-Trichloro-2-hydroxyhydroquinone triethyl ether: unreported.
—— 3,5,6-Trichloro-2-hydroxyhydroquinone triacetate: ndls. from lgr./C_6H_6, m.p. 171° (1). [From $\bar{C}$ with Ac_2O + NaOAc on htg. (1).]

3:4444 (1) Zincke, Schaum, *Ber.* **27**, 557–558 (1894).

3:4450 OCTACHLOROPROPANE (Perchloropropane)



C_3Cl_8 Beil. I - 108, I_1- (35), I_2—

M.P. 160°? (1) B.P. 268–269° at 734 mm. (1)

White extraordinarily pliable (2) crystals, difficult to filter with suction (because of their high vapor pressure (3)) and best purified by fractional distn. (3) or slow sublimation in vac. (2). — Very sol. in alc., ether, or lgr. (1).

[For prepn. of $\bar{C}$ (100% yield (3)) from 1,1,1,2,2,3,3-heptachloropropane (3:0200) by conversion with MeOH/KOH by loss of HCl to 1,1,1,2,3,3-hexachloropropene-2 (3:6370) and subsequent treatment with Cl_2 below 50° in sunlight see (3) (2).] [For formn. from 1,2,3-trichloropropane (3:5840) or from isobutyl chloride (3:7135) with excess ICl_3 at 200° see (1).]

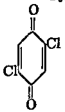
$\bar{C}$ on htg. at 300° (1) or on htg. with $AlCl_3$ (2) splits quantitatively (2) into CCl_4 (3:5100) + tetrachloroethylene (3:5460).

[For fluorination of $\bar{C}$ see (3) (4); for use of $\bar{C}$ + Zn for production of smoke see (5) (6).]

3:4450 (1) Krafft, Merz, *Ber.* **8**, 1296–1302 (1875). (2) Prins, *J. prakt. Chem.* (2) **89**, 416–417 (1914). (3) Henne, Ladd, *J. Am. Chem. Soc.* **60**, 2494 (19[illegible] (4) [illegible] Brit. 378,324, Aug. 11, 1932; French 730,370, Aug. 11, 19[illegible] (1933). (5) Métivier, *Chimie & industrie*, Spec. No. 179 [illegible] (6) Métivier, French 649,853, Dec. 28, 1928; *Cent.* **1931**, I [illegible]

3:4470 2,5-DICHLOROBENZOQUINONE-1,4 (*p*-Dichlorobenzoquinone)

$C_6H_2O_2Cl_2$ Beil. VII - 632, VII_1-(346)



M.P.	**161–162°**	(1)
	160.4–161.4°	(2)
	161° u.c.	(3)
	161°	(4) (17) (28)
	159°	(5) (10)
	158.5°	(6)
	158–161°	(7)

[*See also* 2,5-*dichlorohydroquinone* (3:4690).]

Dark yellow cryst. from alc. or C_6H_6; insol. aq.; alm. insol. cold dil. alc., eas. sol. boilg. abs. alc.; fairly eas. sol. ether or $CHCl_3$. — Volatile with steam; sublimes in vacuum.

[For prepn. of $\bar{C}$ from 2,5-dichlorohydroquinone (3:4690) by oxidn. with $K_2Cr_2O_7$ or

$Na_2Cr_2O_7$ + dil. H_2SO_4 (2) (4) (6) (8) (9) or with conc. HNO_3 at ord. temp (5) see indic. refs.; from 2,5-dichlorohydroquinone dimethyl ether with fumg. HNO_3 in the cold see (1); from 2-chlorobenzoquinone-1,4 (3:1100) via conversion with HCl to 2,5-dichlorohydroquinone (3:4690) and subsequent oxidn. of latter see (5) (17); from 2,5-dichloroaniline [Beil. XII-625, XII_1-(311)] with CrO_3 (5) or from 2,5-dichloro-p-phenylenediamine [Beil. XIII-118] with CrO_3 (10) or $K_2Cr_2O_7$ + dil. H_2SO_4 (28) see indic. refs.; for formn. of $\bar{C}$ from benzoquinone-1,4 (1:9025) in CCl_4 with ICl on gentle warmg. see (3); from benzene with ClO_2 see (11), from copper salt of quinic acid [Beil. X-535, X_1-(270)] by oxidn. with MnO_2 + NaCl + H_2SO_4 see (12).]

[For study of oxidn.-reductn. potential of system $\bar{C}$ + 2,5-dichlorohydroquinone (3:4690) see (6) (13) (14).] — [For use as vulcanization accelerator see (15); for use in prepn of curhodol dyes see (16), for study of bactericidal actn. see (18).]

[$\bar{C}$ is sol in conc. H_2SO_4 with greenish-yellow color, in dimethylaniline with deep blue color (19), $\bar{C}$ is sol in dil. aq alk. with brown color and decomposition (11) (12).]

[$\bar{C}$ with KCN in 85% MeOH gives (20) a ruby-red soln. with red fluorescence; $\bar{C}$ with diphenylketene in ether + pet. eth. gives a compound, m p. 180–192° dec. (21).]

$\bar{C}$ in aq reduces with SO_2 (12) to 2,5-dichlorohydroquinone (3:4690) q.v. (note that the intermediate quinhydrone, dark violet pr. or greenish-black ndls. with 2 H_2O (12), crystal water lost over H_2SO_4 or on warming giving yellow anhydrous form, m.p. 140–145° (22), is known), however, $\bar{C}$ in dil. aq. NaOH (under N_2) treated with SO_2 is in part reduced to 2,5-dichlorohydroquinone (3:4690) and in part sulfonated to mono- and disulfonic acids of $\bar{C}$ (23).

[$\bar{C}$ in $CHCl_3$ at low temps. does not react with Cl_2; at ord. temps , however, yields tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) (24). — $\bar{C}$ in AcOH at 70–80° with 2 moles Br_2 *gives (alm quant. yield (4)) (25) (9) 2,5-dichloro-3,6-dibromobenzoquinone-1,4 [Beil. VII-642]*, golden-brown tbls. from C_6H_6, m p. 292° (4).]

[$\bar{C}$ with conc HCl gives on boilg. (5) 2,3,5-trichlorobenzoquinone-1,4 (3:4672), but some tetrachlorobenzoquinone (chloranil) (3:4978) is also formed.]

$\bar{C}$ (1 pt) in Ac_2O (5 pts.) + AcOH (5 pts.) loses color on boilg. with Zn dust (1) and yields (by reductive acylation) 2,5-dichlorohydroquinone diacetate, cryst. from alc., m p. 141° (1)

$\bar{C}$ (1 pt.) in hot AcOH (40 pts) + conc. HCl (0.4–0.5 pt) treated with aniline (0.4–0.5 pt) yields mainly (26) 2,5-dichloro-3-anilinobenzoquinone-1,4 [Beil XIV-137], blue lfts., m.p 180° (26), and 2,5-dichlorohydroquinone (3:4690) accompanied by small amts. of 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 (see below); $\bar{C}$ htd. with excess aniline yields (26) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil XIV-144], *yel.-br. tbls. from* C_6H_6, m p 290° (26), and 2,5-dichlorohydroquinone (3:4690).

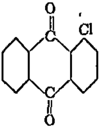
[$\bar{C}$ in C_6H_6 + alc. warmed with slightly more than 1 mole $NH_2OH.HCl$ yields (8) (27) 2,5-dichlorobenzoquinone-1,4 monoxime (2,5-dichloro-4-nitrosophenol) [Beil. VII-633], pale yel. cryst from C_6H_6, m p 155–160° (8) (purified by conv. with Ac_2O + NaOAc to its acetate, yel pr from C_6H_6, m p. 149° (8), and subsequent hydrolysis with NaOH). — $\bar{C}$ in alc. with excess $NH_2OH.HCl$ yields (27) 2,5-dichlorobenzoquinone-1,4 dioxime, grayish yel. cryst. from C_6H_6. m.p not stated (27).]

3:4470 (1) Kohn, Gurewitsch, *Monatsh.* **56**, 135–136 (1930). (2) Hammick, Hampson, Jenkins, *J Chem. Soc* **1938**, 1264 (3) Jackson, Bolton, *J. Am Chem. Soc.* **36**, 1484 (1914). (4) Ling, *J Chem Soc* **61**, 558–559, 563–566, 572–576 (1892). (5) Levy, Schultz, *Ann.* **210**, 150–153 (1881) (6) Conant, Fieser, *J. Am. Chem Soc.* **45**, 2205–2206 (1923). (7) Pfeiffer, *Ann.* **412**, 292–293 (1916) (8) Kehrmann, Grab, *Ann* **303**, 12–14 (1898). (9) Hantzsch, Schniter, *Ber.* **20**, 2279–2282 (1887) (10) Mohlau, *Ber.* **19**, 2010 (1886).

(11) Carius, *Ann* **143**, 316 (1867). (12) Städeler, *Ann.* **69**, 309–312 (1849). (13) Hunter, Kvalnes, *J Am Chem Soc.* **54**, 2574–2575, 2578 (1932). (14) Kvalnes, *J. Am. Chem. Soc.* **56**,

667–670 (1934). (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, I 3133. (16) Herzberg, Hoppe (to A.G.F.A.) Ger. 368,171, Feb. 3, 1923; *Cent.* **1923**, II 1187. (17) Den Hollander, *Rec. trav. chim.* **39**, 482 (1920). (18) Morgan, Cooper, *J. Soc. Chem. Ind.* **43**-T, 352–354 (1924). (19) Pfeiffer, Böttler, *Ber.* **51**, 1828–1829 (1918). (20) Richter, *Ber.* **44**, 3472 (1911).

(21) Staudinger, Bereza, *Ann.* **380**, 261–262 (1911). (22) Ling, Baker, *J. Chem. Soc.* **63**, 1319–1321 (1893). (23) Dodgson, *J. Chem. Soc.* **1930**, 2498–2502. (24) Oliveri-Tortorici, *Gazz. chim. ital* **27**, II 585–586 (1897). (25) Levy, *Ber.* **18**, 2367–2368 (1885). (26) Niemeyer, *Ann.* **228**, 329–334 (1885). (27) Kehrmann, *Ber.* **21**, 3319 (1888). (28) Nason, *J. Am. Chem. Soc.* **40**, 1605 (1918).

3:4480 1-CHLOROANTHRAQUINONE  $C_{14}H_7O_2Cl$ Beil. VII - 787 VII_1-(409)

M.P.	**164°**	(1)	**M.P.**	**161° cor.**	(12)
	162–163°	(2)	*(contd.)*	**161°**	(13)
	162.5° cor.	(3)		**160.4–161.0°**	(14)
	162° cor.	(4) (5) (6)		**160°**	(15) (16)
	162°	(7) (8) (9) (10) (11)		**159.5°–160°**	(17)
	161–162° cor.	(3)		**159°**	(18)

[*See also* 2-*chloroanthraquinone* (3:4922).]

Yellow ndls. from C_6H_6, toluene, or alc.; eas. sol. C_6H_6, toluene, AcOH, nitrobenzene, or AmOH on htg.; spar. sol. alc. or lgr.

[For f.p./compn. data and diagram of system $\bar{C}$ + 2-chloroanthraquinone (3:4922) (eutectic, m.p. 143.9–144.2°, contg. about 25% $\bar{C}$) see (14).]

[For use in coloring oils, fats, and waxes see (19); $\bar{C}$ is very widely used as intermed. in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of $\bar{C}$ from potassium salt of anthraquinonesulfonic acid-1 [Beil. XI-335, XI_1-(81)] by htg with strong HCl + $NaClO_3$ (yields: 97–98% (3), 95% (4)) at 100° (3) (4) (10) (6) (8) (for use of this method in detn. of mixt. of anthraquinone-α- and β-sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of $\bar{C}$ + 2-chloroanthraquinone (3:4922) see (4)) or by actn of Cl_2 at 100° (20) see indic. refs.; from anthraquinonesulfonic acid-1 (9) or its Na salt (15) in dil. HCl on exposure to light see indic. refs.; from anthraquinonecarboxylic acid-1 with HCl + $KClO_3$ in s.t. at 200° for 12 hrs. see (22); from Na salt of anthracenesulfonic acid-1 [Beil. XI-194, XI_1-(44)] with HCl + $NaClO_3$ at 100° see (21); from 1-chloroanthraquinonesulfonic acid-5 by electrolysis of alk. soln. see (23); from K salt of anthraquinonesulfonic acid-1 (see above) (24) or from anthraquinonesulfonyl chloride-1 (5) by htg. in s.t. with $SOCl_2$, or from 1-anthraquinonylarsinic acid by 10 hrs. reflux with $SOCl_2$ (67), see indic. refs.]

[For prepn. of $\bar{C}$ from 2-benzoyl-3- (or 6)-chlorobenzoic acid by ring closure with conc. H_2SO_4 see (7) (25).]

[For prepn. of $\bar{C}$ from 1-aminoanthraquinone (see below) via diazotization and use of Cu_2Cl_2 reactn. see (26); from 1-nitroanthraquinone [Beil. VII-791, VII_1-(415)] with Cl_2 in trichlorobenzene soln. at 160–165° see (27); from 1-hydroxyanthraquinone [Beil. VIII-338, $VIII_1$-(650)] with PCl_5 in boilg. nitrobenzene see (28).]

[C̄ on htg. with conc. H_2SO_4 at 200–205° for 9 hrs. rearr. (29) to 2-chloroanthraquinone (3:4922).]

[C̄ on reductn. with Zn dust + conc. aq. NH_4OH under reflux yields (30) 1-chloroanthracene [Beil. V_1-(324)], colorless lfts. from AcOH, m.p. 81–82° (2), 79° (30). — C̄ on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of Pd/$CaCO_3$ followed by access of air to the prod. gives (87% yield (31)) anthraquinone (1:9095). — C̄ on reductn. with Al powder + conc. H_2SO_4 (32) (33) (6) (34) yields 1-chloroanthrone-9, yel. ndls from $CHCl_3$ + lt. pet., m.p. 118° (32), 114° (6); C̄ on reductn. with Sn + HCl in AcOH contg. $PtCl_4$, however, gives the isomeric 4-chloroanthrone-9, yel. ndls. from $CHCl_3$ + lt. pet., m.p. 118° (32) (note that although these two isomeric chloroanthrones have the same m.p. yet each depresses the m.p. of the other (32) and the earlier prod. of m.p 106° (33) may have been a mixture). — For studies of oxidn.-reductn. potential of C̄ see (12) (17).]

[C̄ with MeOH/KOH at 80° yields (35) 1-methoxyanthraquinone [Beil. VIII-[illegible], $VIII_1$-(651)], m.p. 169 5° — C̄ with 2-hydroxyanthraquinone + NaOAc + Cu powder in boilg. nitrobenzene gives (36) 1,2'-dianthraquinonyl ether [Beil VIII-34[illegible], but m.p. [illegible] not reported. — C̄ with K xanthate + Cu powder boiled for 24 hrs. in AmOH or C̄ with alk. trithiocarbonate in boilg. nitrobenzene (4[illegible]) gives (64% yield (37)) di-(1-anthraquinonyl) sulfide, red pr. from pyridine, m.p. [illegible] (37) (for disulfide see below). — C̄ with thiosalicylic acid (2-mercaptobenzoic acid) + solid KOH htd. in AmOH at 1[illegible]° for [illegible] hrs. gives (96% yield (38)) *S*-(1-anthraquinonyl)-thiosalicylic acid [Beil. [illegible]], [illegible] tbls. from alc., m p. 261° cor. (38); this prod. on htg. with PCl_5 in nitrobenzene gives (98% yield (38)) 3,4-phthalylthioxanthone [Beil. $XVII_1$-(290)], or.-red lfts., m.p. 340° cor. (38).]

[C̄ with NaOH + glycerol htd. at [illegible]° is claimed (39) to yield anthraquinone (1:9095). — C̄ on boilg. with [illegible] + Na_2S_2 (42) yields 1-mercaptoanthraquinone [Beil. [illegible]] [illegible] AcOH, m p. 187° (41); this prod. on oxidn. by air [illegible] (4[illegible]) readily yields di-(1,1'-dianthraquinonyl) di-sulfide, m p. 359° (45), also obtd. from C̄ with Na_2S + S in boilg. alc. (40) (43) (4[illegible]) from C̄ + K thiobenzoate in boilg. AmOH (80% yield (4[illegible])). — C̄ with K_2Se in [illegible] at 80° gives (47) 1-selenomercaptoanthraquinone, or.-red lfts. from AcOH, m.p. [illegible]; also di-(1-anthraquinonyl) diselenide.]

[C̄ with conc. aq. NH_4OH in pres. of Cu salts under press. at elevated temp. [illegible] (50) (57) in alm. quant. yield 1-aminoanthraquinone [Beil. XIV-177, [illegible]] [illegible] ndls., m.p. 242°. — Countless other analogous combinations of C̄ with prim. [illegible] amines cannot be included here; however, note that C̄ with 1-aminoanthraquinone [illegible] + NaOAc + $CuCl_2$ htd. in nitrobenzene yields (52) cf. (51) di-(1-anthraquinonyl)amine [Beil. XIV-180, [illegible]], the prototype of a large group of dyes and dye intermediates (for amplification of this topic see [illegible]). — C̄ with hydrazine hydrate + [illegible] for ½ hr. gives ([illegible] yield ([illegible])) 1-hydrazinoanthraquinone [Beil. [illegible]] [illegible] lfts. from xylene, m.p. [illegible] cor. (54). — For reactn. of C̄ with $NH_2OH.HCl$ [illegible] see (1).]

[For condens. of C̄ with [illegible]-aminoazobenzene (54) or with [illegible] prods. as dyes [illegible] in pres. of [illegible] for prepn. of dyestuffs see (55).]

[C̄ with Cu [illegible] at [illegible] or in boilg. nitrobenzene [illegible] *bis*-1,1'-[illegible] [Beil. VII-[illegible], VII_1-(4[illegible])] [illegible] m.p. 4[illegible] [illegible] quin[illegible] (56); note however [illegible] (51% yield [illegible] (5[illegible])). — C̄ with [illegible] [illegible] 9,10-diphenyl[illegible]

185° (57), 180–182° (58); a mixt. of this prod. with corresp. prod. (m.p. 193°) from 2-chloroanthraquinone (3:4922) has m.p. 152–160° (58).]

[For formn. of addn. cpds. of C̄ with $SbCl_5$ in $CHCl_3$ see (16) (18); for formn. of 1-anthraquinonylpyridinium chloride from C̄ + $AlCl_3$ in pyridine see (59).]

[C̄ on mononitration by soln. in 10 wt. pts. conc. H_2SO_4 and addn. of HNO_3/H_2SO_4 as directed (61) (62) gives (30% yield (61)) 1-chloro-4-nitroanthraquinone [Beil. VII-792, VII_1-(415)], cryst. from AcOH, m.p. 260–261° (63), 259° (61); note that 1-chloro-2-nitroanthraquinone (prepared by indirect means) has m.p. 257–258° (63). — For study of kinetics of nitration of C̄ see (64).]

[C̄ on monosulfonation, e.g., with fumg. H_2SO_4 (20% SO_3) at 160° for 4 hrs. (65) (66), yields a mixt. of about equal parts of two monosulfonic acids eas. separable via their sodium salts; viz., 1-chloroanthraquinonesulfonic acid-6 (Na salt *less* sol. boilg. aq., corresp. sulfonyl chloride, pale yel. pr. from lgr., m.p. 207–208° dec.) and 1-chloroanthraquinonesulfonic acid-7 (Na salt *more* sol. boilg. aq., corresp. sulfonyl chloride, lemon-yel. pl. from C_6H_6, m.p. 200–201° dec.); the m.p. of mixts. of the two sulfonyl chlorides is depressed below 180° (65). — *C̄ on sulfonation in the pres. of Hg salts but otherwise as above yields*, however, a different result as the principal prod. is 1-chloroanthraquinonesulfonic acid-5 (corresp. sulfonyl chloride, yel. pl. from toluene, m p. 243–244° dec. (65) (66)), accompanied by 1-chloroanthraquinonedisulfonic acid-4,5.

3:4480 (1) French, Achenbach, *Ber.* **43**, 3255–3256 (1910). (2) Schilling, *Ber.* **46**, 1066–1069 (1913). (3) Scott, Allen, *Org. Syntheses*, Coll. [illegible]). (4) Ullmann, Ochsner, *Ann.* **381**, 2–6 (1911). [illegible] Maki, *J. Soc. Chem. Ind. Japan*, Suppl. bindi [illegible] Dougherty, Gleason, *J. Am. Chem. Soc.* **52**, 1[illegible] *Chem.* **45**, 19 (1932). (9) Eckert, *Ber.* **60**, 1[illegible] (1927).

(11) Keimatsu, Hirano, Tanabe, *J. Pharm. Soc. Japan* **49**, 531–541 (1929); *Cent.* **1929**, II 1536–1537; *C.A.* **23**, 4696–4697 (1929). (12) Conant, Fieser, *J. Am. Chem. Soc.* **46**, 1873, 1875 (1924). (13) Maki, Nagai, *J. Soc. Chem. Ind. Japan* [illegible] **1936**, I 4905. (14) Coppens, *Rec. trav. chim.* **44**, 91[illegible] (1925). (16) Brass, Tengler, *Ber.* **64**, 1660 (1931). [illegible] 3306 (1940). (18) Brass, Eichler, *Ber.* **67**, 783 (1934). (19) du Pont, Brit. 432,867, Sept. 5, 1935; *Cent.* **1935**, II 3996. (20) Bayer and Co., Ger. 205,195, Dec. 28, 1908; *Cent.* **1909**, I 414.

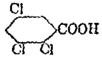
(21) B.A.S.F., Ger. 228,876, Nov. 25, 1910, *Cent.* **1911**, I 102. (22) Day, *J. Chem. Soc.* **1939**, 818. (23) *British Dyestuffs Corp. & Hailwood, Brit. 273,043, July 21, 1927; French 626,669, Sept. 16, 1927*; *Cent.* **1928**, II 2286. (24) M.L.B., Ger. 267,544, Nov. 20, 1913; *Cent.* **1914**, I 89. (25) Imperial Chem. Ind. Ltd. and Loveluck, Thomson & Thomas, Brit. 356,728, Oct. 8, 1931; French 718,333, Jan. 23, 1932. (26) Bayer and Co., Ger. 131,538, May 23, 1902; *Cent.* **1902**, I 1342. (27) B.A S F., Ger. 252,578, Oct. 23, 1912; *Cent.* **1912**, II 1708. (28) A.G.F.A., Ger. 290,879, March 21, 1916; *Cent.* **1916**, I 686. (29) Atack, Clough, Brit. 169,732, Nov. 3, 1921; *Cent.* **1922**, IV 377. (30) *Fischer, Ziegler, J. prakt. Chem. (2) 86, 293–294 (1912).*

(31) Busch, Weber, Zink, *J. prakt. Chem.* (2) **155**, 167 (1940). (32) Barnett, Matthews, [illegible] maschek, *Monatsh.* **39**, 847 (1918). (34) [illegible] Ger. 229,316, Dec. 13, 1910; *Cent.* **1911**, [illegible] *ent.* **1909**, I 2104. (37) Perkin, Sewell, [illegible] Knecht, *Ber.* **44**, 3126–3127 (1911); Ger. [illegible] mura, Maeda, *J. Soc. Chem. Ind. Japan*, [illegible] *C.A.* **32**, 7447 (1938). (40) Bayer and [illegible] 388.

(41) Bayer and [illegible] 204,772, Dec. 3, [illegible] *Cent.* **1933**, II 1764; *C.A.* **27**, 1893 (1933); U.S.

(52) Bayer and Co., Ger. " Das Anthracene und die -470. (54) Imperial Chem. 23 (1938). (55) I.G., Brit. 7, II 4394. (56) Ullmann, shire, *J. Chem. Soc.* **1927,** 1728. (58) E. Bergm (59) Miegs, Heidenreich (to I.G.), perial Chem. Ind. Ltd., Hallwood, (61) Eckert, Steine and Co., Ger. *137,782, Dec. 15, 190* *5, 1922; Cent.* **1923,** II 1029-1030. 35-342 (1911); *C.A.* **36,** 4814-4815 9-1780 (66) Thorpe, Goldberg, B (67) Steinkopf, Schmidt, *Ber.* **61,** 677 (1928).

3:4485 2,3,5-TRICHLOROBENZOIC ACID $C_7H_3O_2Cl_3$ Beil. IX - 345 IX_1—



M.P. 163° (1)
162° (2) (3)

Ndls. from hot aq. (2). — Not volatile with steam. — Very spar. sol. cold aq. but sol. in org solv.

[For prepn. of Č from 2,3,5-trichlorotoluene (3:0610) by oxidn with 20% HNO_3 in s.t. at 140° see (2); from 2,3,5-trichlorobenzaldehyde (3:1060) by oxidn. with $KMnO_4$ see (3), for prepn. from corresp nitrile by hydrolysis see (1).]

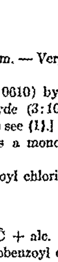
Č on soln. in warm fumg HNO_3 readily yields a mononitro cpd, 2,3,5-trichloro-*x*-nitrobenzoic acid, cryst from alc, m p. 158° (1).

Č with excess PCl_5 yields (1) 2,3,5-trichlorobenzoyl chloride, cryst. from EtOAc, m.p. 36° (1).

—— *Methyl 2,3,5-trichlorobenzoate:* unrecorded.
—— **Ethyl 2,3,5-trichlorobenzoate:** oil. [From Č + alc. + HCl (1).]
Ⓓ **2,3,5-Trichlorobenzamide:** from 2,3,5-trichlorobenzoyl chloride + $(NH_4)_2CO_3$; ndls. from dil. AcOH, m.p 204-205° (1).
—— **2,3,5-Trichlorobenzanilide:** unrecorded.

3:4485 (1) Matthews, *J. Chem. Soc.* **79,** 43-49 (1901). (2) Cohen, Dakin, *J. Chem. Soc.* **81,** 1331 (1902). (3) Hodgson, Beard, *J. Chem. Soc.* **1927,** 2382.

3:4492 5-CHLORONAPHTHOQUINONE-1,4 $C_{10}H_5O_2Cl$ Beil. S.N. 674



M.P. 163° (1)

Yellow ndls. from alc or lgr. — Sublimes undecomposed. — Fairly eas. sol. AcOH or lgr.; moderately sol alc.; spar. sol. aq.

[For prepn. of Č from 5-chloro-1,4-diaminonaphthalene (5-chloronaphthylenediamine-1,2) by oxidn of its hydrochloride with $FeCl_3$ see (1).]

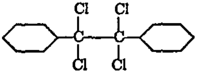
[Č with aniline (no details) gives (1) 2(3?)-anilino-5-chloronapthoquinone-1,4, red

bronzy ndls. from AcOH, m.p. 219° (1); note also that C̄ with aniline boiled for 1 hr. gives (1) a halogen-free cpd., dark violet cryst. from alc., m.p. 140°, but its structure has not been determined.]

3:4492 (1) Fries, Köhler, *Ber.* **57**, 504–505 (1924).

3:4496 1,1,2,2-TETRACHLORO-1,2-DIPHENYLETHANE ($\alpha,\alpha,\alpha',\alpha'$-Tetrachlorobibenzyl; tolane tetrachloride)

$C_{14}H_{10}Cl_4$ Beil. V - 601; V_1-(282); V_2-(507)



M.P. 163°	(1) (2) (3)
162–163°	(4)
162°	(5) (6)
161–162°	(7)
161.5°	(8)
161°	(9)

Colorless cryst. from AcOH, pet. ether, C_6H_6, or toluene. — Eas. sol. boilg. C_6H_6; moderately sol. hot but spar. sol. cold pet. ether; spar. sol. alc. or ether.

C̄ with *trans*-tolane dichloride (3:4210) forms an isomorphous mixt. (8) formerly erroneously regarded as an individual cpd. designated as "ditolane hexachloride."

PREPARATION OF C̄

From Dinuclear Initial Materials

[For prepn. of C̄ from benzil (1:9015) with excess PCl_5 (32% yield (10)) in s.t. at 200° for 6–7 hrs. (5), or from *ms*-dichlorodesoxybenzoin ("chlorobenzil") [Beil. VII-436, VII_1-(234)] with PCl_5 in s.t. at 200° (11) in $POCl_3$ [illegible] refs.; from diphenylacetylene (tolane) [Beil. V-65 [illegible] (13) or from either *cis*-(3:1380) or *trans*-(3:4210) [illegible] refs.]

From Mononuclear Initial Materials

From benzotrichloride. [For prepn. of C̄ from benzotrichloride (3:6540) by reduction in alc. with H_2 + colloidal Pd (75% yield (4)) or H_2 + $Pd/BaCO_3$ (14) in alc.-alkali, or by htg. with Cu powder at 100° (6) or in C_6H_6 under reflux for 4 hrs. (30–36% yield (5)) (1) cf. (10), see indic. refs.; for formn. of C̄ from benzotrichloride (3:6540) with excess dilute (0.2 *N*) MeMgCl in ether (7), with EtMgBr (3) or C_6H_5MgBr (3), or by pyrolysis over hot Pt (15), or by htg. with Ni in atm. of CO_2 (16) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

[C̄ on reduction with conc. HI + P (1) or with H_2 in alc.-alk. + $Pd/CaCO_3$ (14) gives bibenzyl (1:7149), m.p. 52°.]

[C̄ on removal of two adjacent chlorine atoms with Fe powder in boilg. AcOH (12) cf. (5), with Cu powder at 160° (6), with excess conc. (2 *N*) MeMgCl in ether refluxed 4 hrs. (7), with H_2 + hydrazine hydrate in MeOH/KOH 1½ hrs. at b.p. (17), or with Zn dust in boilg. alc. (18) (5) (2) (10) gives either or both *trans*- (3:4210) and *cis*- (3:1380) tolane dichlorides; note that use of insufficient Zn gives (8) cf. (5) (10) the *cis*-tolane dichloride (3:1380) + an isomorphous mixt. of C̄ + *trans*-tolane dichloride (3:4210).]

[C̄ with Na/Hg in alc. gives (11) diphenylacetylene (tolane) (see ref. above), some stilbene (1:7250) and bibenzyl (1:7149) also being formed (2). C̄ on htg. with Zn dust gives (2) stilbene (1:7250).]

[C̄ is very resistant to hydrolysis and is unattacked by H_2O, alc., or AcOH in s.t. at 200° (2); note, however, that C̄ with AcOH in s.t. at 230–250° or with H_2SO_4 at 165° is claimed (2) to give benzil (1:9015).]

[C̄ is very resistant to action of boilg. HNO_3 (2); note, however, that *p,p'*-dinitrotolane dichloride, m.p. 264–265° dec., has been prepd. indirectly (19) (from *p*-nitrobenzal(di)-chloride with acetone + KOH).]

[C̄ with anhydrous HF at 100° yields (20) 1,2-difluoro-1,2-diphenylethylene, m.p. 122–123° (20); however, C̄ with HF in pres. of HgO gives (20) 1,2-dichloro-1,2-difluoro-1,2-diphenylethane, m.p. 128–130° (20).]

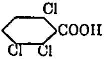
3:4496 (1) Hanhart, *Ber.* **15**, 901 (1882) (2) Liebermann, Homeyer, *Ber.* **12**, 1971–1973 (1879). (3) Sanna, *Ren*
5833 (1939).
(1888) *(6) C*
722–723 (1933). (8) Marckwald, Karczag, *Ber.* **40**, 2994–2996 (1907). (9) Davidson, *J. Am. Chem. Soc.* **40**, 399 (1918) (10) Elloart, *Am. Chem. J.* **12**, 231–232 (1890).

(11) Zinin, *Compt rend.* **67**, 720 (1868), *Ann* **149**, 375 (1869). (12) Lachowicz, *Ber.* **17**, 1164–1165 (1884). (13) Redsko, *J. Russ. Phys.-Chem. Soc.* **21**, 426 (1889); *Ber.* **22**, Referate 760 (1889). (14) Busch, Stöve, *Ber.* **49**, 1067–1068 (1916). (15) Loeb, *Ber.* **36**, 3060–3061 (1903). (16) Korczynski, Reinholz, Schmidt, *Roczniki Chem.* **9**, 731–740 (1929); *C.A.* **24**, 1858 (1930). (17) Busch, Weber, *J. prakt. Chem* (2) **146**, 51–52 (1936) (18) Zinin, *Ber.* **4**, 289 (1871). (19) Olivier, Weber, *Rec. trav. chim.* **53**, 889–890 (1934). (20) Balon, Tinker (to du Pont Co.), U.S. 2,238,242, April 15, 1941; *Cent.* **1942**, I 2328; [*C.A.* **35**, 4779 (1941)].

CHAPTER XI

DIVISION A. SOLIDS

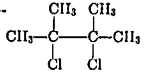
(3:4500–3:4900)

3:4500 2,3,6-TRICHLOROBENZOIC ACID  $C_7H_3O_2Cl_3$ Beil. IX - 345 IX_1—

M.P. 163–164° (1)
163–165° (2)

Cryst. from aq. (1).
[For prepn. of C̄ from 2,3,6-trichlorotoluene (3:0625) by oxidn. with HNO_3 see (1) (2).]
No further data on this compd. are recorded.

3:4500 (1) Cohen, Dakin, *J. Chem. Soc.* **81**, 1332 (1902). (2) Feldman, Kopeliowitsch, *Arch. Pharm.* **273**, 491 (1935).

3:4520 2,3-DICHLORO-2,3-DIMETHYL-BUTANE (Tetramethylethylene dichloride)  $C_6H_{12}Cl_2$ Beil. I - 152 I_1— I_2—

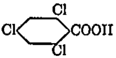
M.P.	**164°**	(1)
	160°	(2)
	159–160°	(3)
	159°	(4)

Colorless cryst. (from alc. (1)) with camphoraceous odor. — Readily sublimes in open tubes on htg.; eas. sol. alc. ether.

[For prepn. of C̄ from tetramethylethylene glycol (pinacol) (1:5805) with fumg. HCl (4) or with PCl_5 (5) see (4) (5); for formn. from 2,3-dimethylbutane (di-isopropyl) (1:8515) with Cl_2 in pres. of I_2 see (4) (6).]

C̄ with alc. KOH in s.t. at 130–140° gives (4) mainly 2,3-dimethylbutadiene-1,3 (1:8050), b.p. 68.7° (accompanied by unsatd. ethers, b.p. 136–146°) (4). [For study of behavior of C̄ with aq. alc. NaOH see (3).]

3:4520 (1) Kahovec, Wagner, *Z. physik. Chem.* **B-47**, 53 (1940). (2) Schorlemmer, *Ann.* **144**, 186–187 (1867). (3) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1380–1388 (1939); *C.A.* **34**, 1611 (1940). (4) Kondakow, *J. prakt. Chem.* (2) **62**, 169–174 (1900). (5) Couturier, *Ann. chim.* (6) **26**, 443–444 (1892). (6) Silva, *Ber.* **6**, 36 (1873).

3:4545 2,4,6-TRICHLOROBENZOIC ACID  $C_7H_3O_2Cl_3$ Beil. IX - 345 IX_1—

M.P.	**164°**	(1)	**M.P.** (*contd.*)	**160–161°**	(3)
	162°	(2)		**160°**	(4) (5)

Long ndls. from hot aq. (4); cryst. from C_6H_6 + pet. eth. — Eas. sol. alc., ether, or $CHCl_3$ (5).

[For prepn. of $\bar{C}$ from 2,4,6-trichloroaniline [Beil. XII-627] via conversion by diazo reactn. to 2,4,6-trichlorobenzonitrile, m.p. 77.5° (1), 75° (6), thence to 2,4,6-trichlorobenzamide (see below) and hydrolysis of latter see (1) (4) (5) (2) (12); for prepn. of $\bar{C}$ from 2,4,6-trichlorotoluene (3:0380) by oxdn. with HNO_3 see (3).]

$\bar{C}$ on soln. in 5 pts conc. HNO_3 yields (1) 2,4,6-trichloro-3-nitrobenzoic acid [Beil. IX-405], cryst. from $CHCl_3$, m p. 160.2° (1)

$\bar{C}$ with PCl_5 (5) (73% yield (2)) or with $SOCl_2$ + pyridine (7) gives 2,4,6-trichlorobenzoyl chloride, b.p 272° (5), 107–107.5° at 6 mm. (2), 120.1–120.4° at 3 mm (7). — This acid chloride is very stable to aq (5) and is alleged to give no ester with MeOH (5). [Note, however, that with EtOH reactn. is 99% complete in 1 min. (7).] [For study of reactn. of 2,4,6-trichlorobenzoyl chloride with MeMgCl (8) or MeMgBr (12) giving (50% yield (2)) di-(2,4,6-trichlorobenzoyl)methane, m p. 160–161°, see (8), with MeMgBr giving 2,4,6-trichloroacetophenone, m p 51° (8) (14), see (8); with C_6H_6 + $AlCl_3$ yielding 2,4,6-trichlorobenzophenone, m p. 103.5°, see (9).]

—— Methyl 2,4,6-trichlorobenzoate: unrecorded. [$\bar{C}$ + MeOH + HCl yields no ester (4) (10).]

—— Ethyl 2,4,6-trichlorobenzoate: unrecorded. [$\bar{C}$ + EtOH + HCl yields no ester (5).]

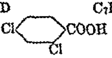
Ⓓ 2,4,6-Trichlorobenzamide: m.p. 181° (1), 177° (6). [This amide has not been recorded as prepd. from the acid chloride + NH_3; it has been obtd. only by partial hydrolysis (11) (6) (1) of 2,4,6-trichlorobenzonitrile (see above).] [The amide itself is only slowly hydrolyzed to $\bar{C}$ by 75% H_2SO_4 at 160° (6), but for conversion to $\bar{C}$ via HNO_2 see (11) (1) (2).]

Ⓓ 2,4,6-Trichlorobenzanilide: from 2,4,6-trichlorobenzoyl chloride + aniline (12), ndls., m.p 197° (12).

3:4545 (1) Montagne, *Rec. trav. chim.* **21**, 383–388 (1902). (2) Fuson, Bertetti, Ross, *J. Am. Chem Soc* **54**, 4381–4382 (1932). (3) Cohen, Dakin, *J Chem. Soc* **81**, 1336 (1902). (4) Meyer, Sudborough, *Ber.* **27**, 3151–3152 (1894). (5) Sudborough, *J. Chem. Soc.* **65**, 1030 (1894). (6) Sudborough, Jackson, Lloyd, *J. Chem. Soc.* **71**, 231–232 (1897). (7) Norris, Ware, *J. Am Chem. Soc.* **61**, 1418–1420 (1939). (8) Ross, Fuson, *J Am. Chem. Soc.* **59**, 1508–1510 (1937). (9) Montagne, *Rec trav chim.* **26**, 279–280 (1907). (10) Meyer, *Ber.* **28**, 1259 (1895).

(11) Sudborough, *J. Chem Soc.* **67**, 602 (1895). (12) Chapman, *J. Chem. Soc.* **1927**, 1749. (13) Fuson, Van Campen, Wolf, *J. Am. Chem. Soc.* **60**, 2269–2270 (1938). (14) Lock, Böck, *Ber.* **70**, 925 (1937).

3:4560 2,4-DICHLOROBENZOIC ACID $C_7H_4O_2Cl_2$ Beil. IX - 342 IX_1-(141)



M.P.	164.3°	(1)	M.P. (*contd.*)	161°	(7)
	164°	(2) (3) (4)		159–160°	(8)
	163–164°	(5)		158°	(9)
	161.5–162.5°	(6)		156–158°	(10)
	161–162°	(20)			

Cryst. from aq., alc. (3), C_6H_6 or C_6H_6 + lgr. — Sublimes undecomposed in ndls. (9) or lfts. (10) — Eas. sol in boilg aq. or org solv. (10).

[For prepn. of $\bar{C}$ from 2,4-dichlorotoluene (3:6290) by oxidn with dil. HNO_3 at 140° (9) (7) (8) or with $KMnO_4$ (70% yield (1)) or by electrolytic oxidn. (65% yield (3)) see indic. refs.; from 2,4-dichlorobenzaldehyde (3:1800) via Cannizzaro reactn. see (5); from 2,4-dichloroaniline [Beil. VII-621] via conversion to and hydrolysis of 2,4-dichlorobenzoni-

trile see (4) (5); from 2,4-dichlorobenzotrichloride with 95% H_2SO_4 see (5) (11) (12); for still other misc. methods see Beil. IX-342 + IX_1-(141).]

$\bar{C}$ warmed at 100° with a mixt. of fumg. HNO_3 (D = 1.52) + conc. H_2SO_4 as directed (13) yields 2,4-dichloro-3,5-dinitrobenzoic acid, pr. from dilute alc., m.p. 210–211° (13), together with a trace of 2,4-dichloro-1,3-dinitrobenzene, m.p. 103°, insol. in Na_2CO_3. [A mononitrated $\bar{C}$, viz., 2,4-dichloro-5-nitrobenzoic acid, cryst. from 30% AcOH, m.p. 161–163° (11), 162° (18), and 2,4-dichloro-6-nitrobenzoic acid, cryst. from C_6H_6, m.p. 189–190° (19), have been prepd. indirectly.]

$\bar{C}$ with PCl_5 (14) or $SOCl_2$ (15) (3) yields 2,4-dichlorobenzoyl chloride, b.p. 150° at 3–4 mm. (14), 152–155° at 30 mm. (16), 91.9–92.5° at 1 mm. (15). [For conv. of this acid chloride to 2,4,2′,4′-tetrachlorodibenzoyl peroxide see (3).]

—— Methyl 2,4-dichlorobenzoate: oil, b.p. 132° at 15 mm., D_{20}^{20} = 1.572 (21). [From $\bar{C}$ by conv. to $Na\bar{A}$ and htg. with MeI in MeOH for 20 hrs. (73% yield (21))].

—— Ethyl 2,4-dichlorobenzoate: constants unrecorded. [For study of rate of hydrolysis see (17).]

—— 2,4-Dichlorobenzamide: unrecorded.

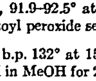
—— 2,4-Dichlorobenzanilide: unrecorded.

3:4560 (1) Bornwater, Holleman, *Rec. trav. chim.* **31**, 226–230 (1912). (2) Lock, Böck, *Ber.* **70**, 923 (1937). (3) Fichter, Adler, *Helv. Chim. Acta* **9**, 286–287 (1926). (4) Gomberg, Cone, *Ann.* **370**, 183 (1909). (5) van der Lande, *Rec. trav. chim.* **51**, 103 (1932). (6) Gassmann, Hartmann, *J. Am. Chem. Soc.* **63**, 2394 (1941). (7) Wynne, *J. Chem. Soc.* **1936**, 703. (8) Cohen, Dakin, *J. Chem. Soc.* **79**, 1129 (1901). (9) Lellmann, Klotz, *Ann.* **231**, 315–316 (1885). (10) Krauss, *Ber.* **37**, 221 (1904).

(11) Villiger, *Ber.* **61**, 2598 (1928). (12) Ger. 234,290, May 4, 1911; *Cent.* **1911**, I 1567. (13) Borsche, Bahr, *Ann.* **402**, 90–91 (1914). (14) Cohen, Briggs, *J. Chem. Soc.* **83**, 1213–1214 (1903). (15) Norris, Ware, *J. Am. Chem. Soc.* **61**, 1418 (1939). (16) B.A.S.F. Ger. 331,696, Jan. 10, 1921 [*C.A.* **15**, 2102 (1921)]. (17) Blakey, McCombie, Sudborough, *J. Chem. Soc.* **1926**, 2863–2868. (18) Grimm, Günther, Tittus, *Z. physik. Chem.* **B-14**, 184 (1931). (19) Ruggli, Zaeslin, *Helv. Chim. Acta* **19**, 439 (1936). (20) Roberts, Turner, *J. Chem. Soc.* **1927**, 1846.

(21) Samant, *Ber.* **75**, 1011 (1942).

3:4580 3,5-DICHLOROPHTHALIC ACID $C_8H_4O_4Cl_2$ Beil. IX - 817 IX_1—



M.P. 164° (1)
164° dec. (2)

[*See also 3,5-dichlorophthalic anhydride* (3:2375).]

Colorless ndls. or tbls. from aq. HCl; readily sol. in cold alc., ether, or acetone, but spar. sol. in C_6H_6 or $CHCl_3$ even on boilg.

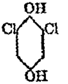
[For prepn. of $\bar{C}$ from 3,5-dichlorophthalic anhydride (3:2375) on boilg. with aq. see (1) (2); from aq. soln. of $NH_4H\bar{A}$ by passing in HCl gas see (1) (2); from 3,5-dichloro-1,2-dimethylbenzene [Beil. V-364] (itself obtd. in good yield from dimethyldihydroresorcinol ("methone") (1:0768) with PCl_5 in $CHCl_3$ (2) (3)) by oxidn. with dil. HNO_3 in s.t. at 190–200° see (2).]

Salts. $NH_4H\bar{A}$, spar. sol. aq., eas. prepd. by mixing aq. solns. of $(NH_4)_2\bar{A}$ + $\bar{C}$; $Ag_2\bar{A}$, white curdy ppt. from warm aq. soln. of $(NH_4)_2\bar{A}$ by addn. of aq. $AgNO_3$.

Esters. Dimethyl 3-chlorophthalate and methyl hydrogen 3-chlorophthalate are unreported: diethyl 3-chlorophthalate (from $Ag_2\bar{A}$ with EtI in dry ether) is oil, b.p. 312–313° at 760 mm. (2); ethyl hydrogen phthalate is unreported.

C̄ on htg. alone (1) or with AcCl (2) yields 3,5-dichlorophthalic anhydride (3:2375), m.p. 89°.

3:4580 (1) Waldmann, Schwenk, *Ann* **487**, 293 (1931). (2) Crossley, LeSueur, *J. Chem. Soc.* **81**, 1536–1537 (1902). (3) Crossley, LeSueur, *J. Chem. Soc.* **82**, 826–827 (1902).

3:4600 2,6-DICHLOROHYROQUINONE  $C_6H_4O_2Cl_2$ **Beil. VI - 850**
(*m*-Dichlorohydroquinone) **VI₁-(417)**

M.P.	**165°**	(1)
	164°	(2)
	163–164°	(3)
	163°	(4)
	161–162° cor.	(7)
	161°	(5)
	157–158°	(6)

[*See also* 2,6-*dichlorobenzoquinone*-1,4 (3:3750).]

Colorless lfts from dil. alc.; ndls. from aq. or C_6H_6. — Sublimes

[For prepn. of C̄ from 2,6-dichlorobenzoquinone-1,4 (3:3750) by reductn. with SO_2 in aq. see (80% yield (5)) (6) (7) (note, however, that the quinone in dil. aq NaOH under N_2 with SO_2 is in part reduced to C̄ and in part sulfonated to mono- and disulfonic acids (8)); from 2,4,6-trichlorophenol (3:1673) in 2 *N* H_2SO_4 on electrolytic oxidn. see (4); from 3,5-dichloro-4-hydroxybenzaldehyde (3:4400) in *N* KOH with H_2O_2 see (3); from sodium benzoquinone-1,4-sulfonate with conc. HCl above 20° in CO_2 (below 20° chlorohydroquinonesulfonic acid results) see (1) (9).]

[For use of C̄ as antioxidant and gum inhibitor in cracked gasoline see (10); for use in aq. petroleum emulsion as insecticidal oil spray see (11); for use as vulcanization accelerator see (18).]

C̄ on oxidn. with CrO_3 (12) or with excess aq. $FeCl_3$ on warming (3) yields 2,6-dichlorobenzoquinone-1,4 (3:3750) (the intermediate quinhydrone cpd., brown powder or pr. or dark ndls. (5), m.p. 135° (13), may separate with insufficient oxidant). [For studies on oxidn.-reductn. potential of system: C̄ + 2,6-dichlorobenzoquinone-1,4 (3:3750) see under latter]

[*C̄ in conc.* H_2SO_4 *with chloral hydrate (3:1270) (2 moles) gives (64% yield (14))* 5,7-dichloro-6-hydroxy-2,4-*bis*-(trichloromethyl)benzdioxin-1,3, colorless pl. from boilg. alc., $CHCl_3$, C_6H_6, or pet. eth , m p. 114–115° (14).]

—— **2,6-Dichlorohydroquinone diacetate:** ndls. and pr. from aq alc., m p. 98° (2). 85–86° on rap. htg , 111–113° on slow htg. (15), 75 5° (7), 66 5° (16). (The reasons for these divergences appear never to have been explained.) [From C̄ with Ac_2O (16) (15).]

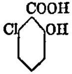
Ⓓ **2,6-Dichlorohydroquinone dibenzoate:** colorless ndls. from alc , m p. 105° (16). [From C̄ on htg with BzCl (16).]

Ⓓ **2,6-Dichlorohydroquinone dimethyl ether:** m p. not reported. [From C̄ in dil. aq. alk. with Me_2SO_4 (17); this prod. with 3–4 pts. cold fumg HNO_3 *nitrates* yielding (17) 2,6-dichloro-3,5-dinitrohydroquinone dimethyl ether, colorless cryst. from alc., m.p. 121–123° (17)]

3:4600 (1) Seyewetz, *Compt. rend.* **156**, 902 (1913). (2) Kehrmann, Tiesler, *J. prakt. Chem.* (2)-**40**, 481 (1889). (3) Dakin, *Am. Chem. J.* **42**, 491 (1909). (4) Fichter, Stocker, *Ber.* **47**, 2016 (1914). (5) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2202–2204 (1923). (6) Faust, *Ann.* **149**, 155 (1869). (7) van Erp, *Ber.* **58**, 665 (1925). (8) Dodgson, *J. Chem. Soc.* **1930**, 2498–2502 (9) Seyewetz, Paris, *Bull. soc. chim.* (4) **13**, 489–490 (1913). (10) Clarke, Towne (to Texas Co), U.S. 2,023,871, Dec. 10, 1935; *Cent.* **1936**, I 2671; *C.A.* **30**, 951 (1936).

(11) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* **1931**, I 2799; *C.A.* **24**, 5928 (1930). (12) Den Hollander, *Rec. trav. chim.* **39**, 481–482 (1920). (13) Ling, Baker, *J. Chem. Soc.* **63**, 1321–1322 (1893). (14) Chattaway, Calvet, *J. Chem. Soc.* **1928**, 2915, 2918. (15) Ling, *J. Chem. Soc.* **61**, 560 (1892). (16) Levy, *Ber.* **16**, 1445–1446 (1883). (17) Kohn, Marberger, *Monatsh.* **45**, 654–656 (1924). (18) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933, *Cent.* **1933**, I 3134.

3:4610 6-CHLORO-2-HYDROXYBENZOIC ACID $C_7H_5O_3Cl$ Beil. X - 104
(6-Chlorosalicylic acid) X_1—



M.P. 166° (1)

Colorless ndls. from aq., grad. turning red in air. — Sol. in aq. and most org. solvents; not volatile with steam.

[For prepn. of C̄ from 6-chloro-2-aminobenzoic acid (6-chloroanthranilic acid) [Beil. XIV-366, XIV_1-(548)] by diazotization and boilg. with aq. (*m*-chlorophenol (3:0255) is also formed) see (1).]

C̄ with $FeCl_3$ soln. gives violet color.

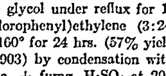
For $NH_4\bar{A}$, $K\bar{A}$, $Ba\bar{A}_2$, $Ag\bar{A}$, all sol. in aq., see (1).

[The methyl ether of C̄, viz., 6-chloro-2-methoxybenzoic acid, m.p. 141° (2), has been obtd. indirectly from 2-chloro-6-methoxytoluene [Beil. VI-359] by $KMnO_4$ oxidn. (2).]

[For esterification of C̄ with glycol monoethers and use of prods. as plasticizers see (3).]

3:4610 (1) Cohn, *Mitt. Technol. Gewerb.-Mus. Wien* **11**, 178–182; *Cent.* **1901**, II 925. (2) Ullmann, Panchaud, *Ann.* **350**, 113 (1906). (3) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374 March 11, 1941; *C.A.* **35**, 3738 (1941).

3:4612 DI-(*p*-CHLOROPHENYL)ACETIC ACID $C_{14}H_{10}O_2Cl_2$ Beil. S.N. 952



M.P. 166.0–166.5° u.c. (1)
163–164° (2)

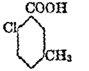
Colorless cryst. from dil. alc. Neut. Eq. = 281.

[For prepn. of C̄ from 1,1,1-trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT") (3:3298) by action of excess $Ba(OH)_2.8H_2O$ in ethylene glycol under reflux for 10–12 hrs. (33% yield) see (1); from 1,1-dichloro-2,2-*bis*-(*p*-chlorophenyl)ethylene (3:2438) by similar treatment (1) or with alc. KOH in s.t. at 150–160° for 24 hrs. (57% yield (2)) see indic. refs.; for prepn. of C̄ from chlorobenzene (3:7903) by condensation with glyoxylic acid monohydrate $(HO)_2CH.COOH$ in pres. of conc. + fumg. H_2SO_4 at 20° (18.6% yield) see (1).]

C̄ with KOH in ethylene glycol refluxed 10–12 hrs. loses CO_2 giving alm. 100% yields (1) of 4,4′-dichlorodiphenylmethane (3:1057), m.p. 55°.

Note that C̄ is one of the metabolitic prods. obtd. from the urine after administration of "DDT" (3:3298) to rabbits.

3:4612 (1) White, Sweeney, *U S. Pub. Health Repts.* **60**, 66–71 (1945). (2) Grummitt, Buck, Jenkins, *J. Am. Chem Soc* **67**, 156 (1945).

3:4615 6-CHLORO-3-METHYLBENZOIC ACID  $C_8H_7O_2Cl$ Beil. IX - 479 IX_1—

M.P. 167° u.c. (1) (2)
163–166° (3)

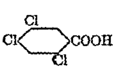
Colorless ndls. from aq. or alc.

[For prepn. of C̄ from 6-chloro-3-methylacetophenone [Beil. VII-307] by oxidn. with $KMnO_4$ or dil. HNO_3 see (1); from β-chloroethyl 6-chloro-3-methylphenyl ketone (2) by oxidn. at 100° with mixt. of equal pts. conc. HNO_3 (D = 1.42) and water see (2); from p-chlorotoluene (3·8287) in CS_2 with oxalyl (di)chloride (3:5060) + $AlCl_3$ for 20 hrs. at room temp. see (3).]

[C̄ with 6 pts. $SOCl_2$ gives (alm. quant. yield (3)) 6-chloro-3-methylbenzoyl chloride, b.p. 165–167° at 85 mm. (3).]

C̄ on oxidn with $KMnO_4$ yields (1) (3) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3·4980), m.p. 286° u c. (1).

3:4615 (1) Claus, *J prakt Chem.* (2) **46**, 27 (1892) (2) Mayer, Müller, *Ber.* **60**, 2281 (1927). (3) Scholl, Meyer, Keller, *Ann.* **513**, 298 (1934).

3:4630 2,4,5-TRICHLOROBENZOIC ACID  $C_7H_3O_2Cl_3$ Beil. IX - 345 IX_1-(141)

M.P. 168° (1)
164–165° (2)
163° (3)
162–164° (4)
160–163° (6)

Ndls. from aq. or dil. alc. — Alm. insol. cold aq , eas. sol. cold abs. alc. (4). — Sublimes in ndls. (4).

[For prepn of C̄ from 1,2,4-trichlorobenzene (3:6420) via nitration, reduction, conversion via diazo reactn. to 2,4,5-trichlorobenzonitrile, m.p. 104° (1), and subsequent indirect hydrolysis see (1); from 2,4,5-trichlorotoluene (3·2100) by oxidn. with HNO_3 (4) (6) or CrO_3 (5) see (4) (5) (6); from 2,4,5-benzotrichloride via htg. with aq. in s.t. at 260° see (3); from 3,4-dichlorobenzoic acid (3:4925) + $Ca(OCl)_2$ see (3); from HNO_3 oxidn. of certain fractions of chlorinated isopropylbenzene (cumene) see (2).]

For salts, viz., $NH_4\bar{A}$, $Ca\bar{A}_2.2H_2O$; $Sr\bar{A}_2.4H_2O$; $Ba\bar{A}_2.7H_2O$, see (3).

C̄ on nitration with hot mixt. of equal vols. conc. HNO_3 + conc. H_2SO_4 yields (3) 2,4,5-trichloro-x-nitrobenzoic acid, ndls. from aq., m.p. 220° (3).

C̄ with PCl_5 (3) or $SOCl_2$ (1) yields 2,4,5-trichlorobenzoyl chloride, b.p. 272° sl. dec. (3), 125° at 2 mm. (1); m.p. abt. 28° (1), 41° (3).

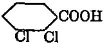
—— Methyl 2,4,5-trichlorobenzoate: unrecorded.

—— Ethyl 2,4,5-trichlorobenzoate: from C̄ + EtOH + HCl (3); m.p. 65° (1) (3).

⊕ 2,4,5-Trichlorobenzamide: from 2,4,5-trichlorobenzoyl chloride + cold conc. NH_4OH (3), ndls. from C_6H_6, m.p. 167.5° (3), 168° (1). [For conversion of this amide to C̄ via HNO_2 see (1).]

3:4630 (1) Baker, Tweed, *J. Chem. Soc.* **1941**, 800.
et Phys. 8, No
(3) Beilstein,
(1902). (5) J
273, 494 (1935).

3:4650 2,3-DICHLOROBENZOIC ACID



$C_7H_4O_2Cl_2$ Beil. IX - 342
IX_1—

M.P. 168.3° cor. (1)
166° (2)
164° (3)
163° (4)

Cryst. from C_6H_6 or from 30% AcOH (1).

[For prepn. of C̄ from 2,3-dichlorotoluene (3:6345) with alk. $KMnO_4$ (1) (2) or with dil. HNO_3 in s.t. at 140° (2) (4) see (1) (2) (4); from benzoic acid (1:0715) by chlorination with $KClO_3$ + HCl (3) (6) or with $Ca(OCl)_2$ (7) see (5) (6) (7).]

For *f.p./compn. data on mixts. of C̄ with 2,5-dichlorobenzoic acid (3:4340), m.p. 154.4°*, see (1).

C̄ on htg. with lime yields (6) *o*-dichlorobenzene (3:6055).

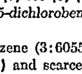
C̄ is unaffected by conc. H_2SO_4 at 300° (6) and scarcely affected by htg. with fumg. HNO_3 (10). — However, C̄ dislvd. in boilg. non-fumg. HNO_3 and treated as directed (10) with conc. H_2SO_4 yields 2,3-dichloro-*x*-nitrobenzoic acid, m.p. 214–215° u.c. (10).

C̄ with PCl_5 yields (8) 2,3-dichlorobenzoyl chloride, b.p. 140° at 14 mm. (8). [This acid chloride is formed during chlorination of benzoyl chloride in presence of $FeCl_3$ where it *constitutes 23% of the dichlorinated fraction* (8).]

—— **Methyl 2,3-dichlorobenzoate**: unrecorded.
—— **Ethyl 2,3-dichlorobenzoate**: m.p. unrecorded. [For study of velocity of hydrolysis see (9).]
—— **2,3-Dichlorobenzamide**: unrecorded.
—— **2,3-Dichlorobenzanilide**: unrecorded.

7, 162 (1887).
hem. Soc. **79**,
–1627 (1887).
(9) Blakey,
Ber. **20**, 1624
(1887).

3:4670 5-CHLORO-2-METHYLBENZOIC ACID



$C_8H_7O_2Cl$ Beil. S.N. 941

M.P. 168.5–169.5° (1)
168° (2)

Colorless ndls. from alc.

Note that the materials of m.p. 130° (3) and 137° (4) formerly supposed to have been ... are now believed (1) to have been mixtures of C̄ with the isomeric 4-chloro-2-methylbenzoic acid (3:4700).

... n 5-chloro-2-methylaniline [Beil. XII-835, XII_1-(384)] via conv. ... onitrile (1) (2), ndls. from pet. ether, m.p. 48° (2), 45–46° (1), and ... with 70% H_2SO_4 (2) see indic. refs]

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[C̄ yields (no details) an acid chloride which with C_6H_6 + $AlCl_3$ in CS_2 gives (2) 5-chloro-2-methylbenzophenone, m.p. 41° (2), b.p. 191° at 12 mm. (2).]

C̄ on oxidn. with $KMnO_4$ yields (1) 4-chlorophthalic acid (3:4390), m.p. 151° (1).

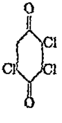
—— Methyl 5-chloro-2-methylbenzoate: unreported.

—— Ethyl 5-chloro-2-methylbenzoate: b.p. unreported, D_4^{20} = 1.1628 (1), $n_{He}^{20.0}$ = 1.52483 (1).

—— 5-Chloro-2-methyl benzamide: unreported.

3:4670 (1) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 16–18 (1929). (2) de Diesbach, Dobbelmann, *Helv. Chim. Acta* **14**, 375 (1931). (3) Claus, Bayer, *Ann.* **274**, 308–309 (1893). (4) Claus, Stapelberg, *Ann.* **274**, 311 (1893).

3:4672 2,3,5-TRICHLOROBENZOQUINONE-1,4



$C_6HO_2Cl_3$ Beil. VII - 634 VII₁-(347)

M.P. 169–170° (1)
168° cor. (2)
165–166° (3) (10) (17)
165° (4)
164–166° (5)
163–164° (22)
163° (30)
162–163° (6) (7)

Yellow lfts. from alcohol; reddish yel. lfts. from $CHCl_3$/lgr. — Insol. cold aq.; spar. sol. cold alc.; eas. sol. hot alc. or ether. — C̄ is sublimable [for study of sublimation press see (8).]

[For studies of heat of formation see (9); for studies of heat of combustion see (10) (11).]

[For studies of bactericidal actn. of C̄ see (12); for patent on use of C̄ as vulcanization accelerator see (13).]

PREPARATION OF C̄

From 2,3,5-trichlorohydroquinone. [For prepn. of C̄ from 2,3,4-trichlorohydroquinone (3:4052) by oxidn., e.g., with CrO_3 at 0° (10), conc. HNO_3 (14) (5) see indic. refs.]

From phenol or chlorinated phenols. [For prepn. of C̄ from phenol (1:1420) via sulfonation followed by oxidn. with $KClO_3$ + HCl see (3) (15) cf. (22), note that by this method both C̄ and 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) are produced; for sepn. of C̄ from latter see (5) (16).]

[For prepn. of C̄ from 2,3,5-trichlorophenol (3:1340) or from 2,3,6-trichlorophenol (3:1160) with fumg. HNO_3 on protracted htg. (17), or from 2,4,6-trichlorophenol (3:1673) with mixt. of conc. HNO_3 + conc. HCl boiled for a few minutes (2), or from 2,3,4,6-tetrachlorophenol (3:1687) by oxidn. with 5 wt. pts. fumg. HNO_3 (70% yield (1)), see indic. refs.]

From amines, aminophenols, etc. [For formn. of C̄ from aniline during electrolytic oxidn. in HCl soln. see (18); from *p*-aminophenol hydrochloride with $Ca(OCl)_2$ soln. see (19); from 2,3,5-trichloro-4-aminophenol hydrochloride by action of Br_2 (20) or NaOBr

(30); from benzal *p*-anisidine or benzal *p*-phenetidine by treatment with *ter*-AmOCl (3:9287) followed by subsequent oxidn. with $K_2Cr_2O_7/H_2SO_4$ see (4).]

From various derivs. of C̄ by hydrolysis. [For formn. of C̄ from various imide derivs. of C̄ by acid hydrolysis, e.g., from the corresp. *N*-(*p*-chlorophenyl)imide [Beil. XII-611] (21), *N*-(2,4,6-trichlorophenyl)imide [Beil. XII-628] (22) (7), or *N*-(2,4-dinitrophenyl)-imide [Beil. XII-754] (23), see indic. refs.]

From miscellaneous sources. [For formn. of C̄ from C_6H_6 (1:7400) by oxidn. with CrO_2Cl_2/AcOH (24), from copper salt of quinic acid [Beil. X-535, X_1-(270)] by oxidn. with MnO_2/NaCl/H_2SO_4 (14), or from benzoquinone-1,4 (1:9025) with Cl_2 (25) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Reduction. C̄ with aq. SO_2 (5) (14) (15) (16), or C̄ in ether soln. with aq. SO_2 (1) reduces to 2,3,5-trichlorohydroquinone (3:4052). [Note that this reaction is used (16) to separate C̄ from 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil") (3:4978) since the latter is but slowly reduced by aq. SO_2.] [For studies of oxidn.-reduction potential of system C̄ + 2,3,5-trichlorohydroquinone (3:4052) see (6) (26) (27).]

Oxidation. C̄ with strong HNO_3 on digestion is degraded with formn. of *trichloronitromethane ("chloropicrin") + CO_2 (15).*

Chlorination. [C̄ with Cl_2 reacts only very slowly; however, C̄ with Cl_2 + I_2 + aq. (15), or C̄ with Cl_2 + HCl (28), gives 2,3,5,6-tetrachloro-benzoquinone-1,4 ("chloranil") (3:4978).]

Reaction with HCl. C̄ with conc. HCl on protracted boilg. (29) (3), or C̄ with fumg. HCl in s.t. at 130° (30), gives 2,3,5,6-tetrachlorohydroquinone (3:4941).

Behavior of C with other inorganic reactants. *With aq. alkali.* [C̄ with dil. aq. KOH turns green and then dis. to a red-brown soln. from which upon acidification is pptd. (5) 2,5-dichloro-3,6-dihyroxybenzoquinone-1,4 ("chloroanilic acid") (3:4970).]

With aq. K_2SO_3. [C̄ dis. in warm aq. K_2SO_3 or $KHSO_3$ and on cooling ppts. (31) the potassium salt of 2,3,5-trichlorohydroquinonesulfonic acid-6 [Beil. XI-300]; the mother liquor conts. a cpd. which on boilg. with KOH gives (31) the salt of 2,5-dihydroxybenzoquinone-1,4-disulfonic acid-3,6 [Beil. XI-353].]

With NH_3. [C̄ with alc. NH_3 reacts vigorously yielding (3) a dark soln. from which can be obtd. in small amt. 3,6-dichloro-2,5-diaminobenzoquinone-1,4 ("chloranilamide") [Beil. XIV-144].]

With PCl_5. [C̄ with PCl_5 + $POCl_3$ in s.t. at 180–200° gives (5) hexachlorobenzene (3:4949).]

Behavior of C with organic reactants. *With phenol.* C̄ with K phenolate (2 moles) at 100° for 20 min. gives (32) 3-chloro-2,5-diphenoxybenzoquinone-1,4, or. tbls. from alc., m.p. 169–170° (32).

With 2,3,5-trichlorohydroquinone. C̄ (1 mole) with 2,3,5-trichlorohydroquinone (1 mole) (3:4052) in $CHCl_3$ soln. gives on evapn. (6) (33) the corresp. quinhydrone, green-black cryst., m.p. 114–115° (6), 103° (33).

With acetyl chloride. C̄ with AcCl in s t. at 160–180° gives (5) 2,3,5,6-tetrachlorohydroquinone diacetate (cf. 3:4941).

With aniline. [C̄ (1 mole) with aniline hydrochloride (1 mole) in AcOH on boilg. and subsequent partial evapn. (34) cf. (35) gives (66.5% yield (34)) 2,3,5-trichloro-6-anilinobenzoquinone-1,4 [Beil XIV-137], blue lfts. from hot alc., but without def. m p. (35).—C̄ with aniline (excess) in alc. (30) (35) or AcOH (35) gives, however, 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV_1-(421)], yel.-brown metallic lfts. from C_6H_6, m.p. 290° (35), 285–290° (30).]

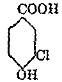
With triphenylphosphine. $\bar{C}$ with 20% soln. of $(C_6H_5)_3P$ in $CHCl_3$ gives (36) wine-red color; note, however, that a very similar behavior is shown by 2,3,5,6-tetrachlorobenzoquinone-1,4 ("chloranil").

3:4672 (1) Biltz, Giese, *Ber.* **37**, 4016–4017 (1904). (2) Leger, *Bull. soc. chim.* (4) **3**, 581–582 (1908). (3) Knapp, Schultz, *Ann* **210**, 174–176, 180–181 (1881) (4) Musante, Fusco, *Gazz chim. ital.* **66**, 647–648 (1936) (5) Graebe, *Ann* **146**, 22–30 (1868). (6) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2206–2207 (1923). (7) Bradfield, Cooper, Orton, *J Chem. Soc.* **1927**, 2858–2859 (8) A. S. Coolidge, M. S. Coolidge, *J Am. Chem Soc* **49**, 101–104 (1927). (9) Sjöström, *Svensk Kem. Tid* **48**, 121–124 (1936), *Cent.* **1937**, I 58, *C.A* **30**, 6634 (1936). (10) Valeur, *Ann. chim* (7) **21**, 496–497 (1900)

(11) Swietoslawski, Starczewska, *J. chim phys* **22**, 399–401 (1925). (12) Morgan, Cooper, *J. Soc Chem Ind* **43**-T, 352–354 (1924). (13) Fisher (to Naugatuck Chem. Co) French 740,978, Feb. 3, 1933, *Cent* **1933** I 3134, *C A* **27**, 2845 (1933). (14) Stadeler, *Ann* **69**, 301, 322 (1849). (15) Stenhouse, *Ann , Suppl* **6**, 209–212, 216–219 (1868). (16) Graebe, *Ann* **263**, 28–30 (1891). (17) Lampert, *J prakt Chem* (2) **33**, 382–383 (1886). (18) Erdelyi, *Ber.* **63**, 1201–1202 (1930). (19) Schmitt, Andresen, *J prakt Chem* (2) **23**, 436–437 (1881). (20) Schmitt, Andresen, *J. prakt. Chem* (2) **24**, 429, 434 (1881).

(21) Jacobson, *Cent.* **1898**, II 36. (22) Orton, Smith, *J. Chem. Soc* **87**, 395–396 (1905). (23) Réverdin, Crepieux, *Ber* **36**, 3268 (1903). (24) Carstanjen, *Ber.* **2**, 633 (1869) (25) Woskresenski, *J prakt. Chem* (1) **18**, 420 (1839). (26) Conant, *J. Am Chem Soc.* **49**, 293–297 (1927). (27) Kvalnes, *J Am Chem. Soc* **56**, 667–670 (1934) (28) Schuloff, Austrian 127,813, April 25, 1932, *Cent* **1932**, II 924, *C A* **26**, 4348 (1932) (29) Levy, Schultz, *Ann.* **210**, 154 (1881) (30) Andresen, *J prakt Chem* (2) **28**, 422–427 (1883).

(31) Graebe, *Ann* **146**, 55–59 (1868). (32) Jackson, Grindley, *Am Chem. J.* **17**, 653–654 (1895) (33) Lang, Baker, *J Chem Soc* **63**, 1322–1323 (1893). (34) Brass, Papp, *Ber.* **53**, 458 (1920) (35) Niemeyer, *Ann* **228**, 337–338 (1885) (36) Schönberg, Ismail, *J. Chem. Soc.* **1940**, 1374–1378

3:4675 3-CHLORO-4-HYDROXYBENZOIC ACID  $C_7H_5O_3Cl$ **Beil. X - 175**
X_1—

M.P. **169–170°** (1) (2)
169° (3)
165–166° (4)
164–165° (5)
164° (6)

Colorless ndls. from aq.; spar. sol. cold but eas. sol. hot aq.; eas. sol. alc., ether; very eas. sol. acetone; spar. sol C_6H_6, $CHCl_3$, lgr. — Sublimes undecomposed. [For study of ioniz. const. at 25° see (9).]

[For prepn. of $\bar{C}$ from *p*-hydroxybenzoic acid (1:0840) with aq. HCl + 30% H_2O_2 (60–90% yield (6)) or in Na_2CO_3 soln. with Cl_2 (100% yield $Na\bar{A}$ (7)), or in AcOH with $KClO_3$ + HCl (8), or with $SbCl_5$ on warming (1), see indic. refs.; from 3-amino-4-hydroxybenzoic acid [Beil. XIV-597] via diazotization and use of Cu_2Cl_2 reactn. see (4); from *o*-chlorophenol (3:5980) in CCl_4 with alc. alk. in s t. at 125–130° see (5); from methyl 3-chloro-4-hydroxybenzoate (see below) by hydrol. with 40% KOH see (2); from 3-chloro-4-hydroxybenzonitrile (3) via hydrol. with acid see (5).]

$\bar{C}$ in aq. soln. gives with $FeCl_3$ a brown ppt. (1).

[$\bar{C}$ with PCl_5 (2 moles) followed by treatment of the intermediate acid chloride with aq. yields (1) 3,4-dichlorobenzoic acid (3:4925); $\bar{C}$ on warming with $SbCl_5$ (2 moles) yields (1) 3,5-dichloro-4-hydroxybenzoic acid (3:4950).]

[For studies of bactericidal actn. of $\bar{C}$ or its derivatives see (10) (11) (12) (13) (14).]

—

Ⓓ Methyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc. or lgr., m.p. 107° (2), 106–107° (4). [From $\bar{C}$ in MeOH with H_2SO_4 (4) or from methyl *p*-hydroxybenzoate (1:1549) with SO_2Cl_2 (2).] [For reactn. of this prod. with acetobromglucose see (10); for studies of bactericidal power see (11).]

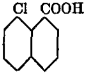
—— Ethyl 3-chloro-4-hydroxybenzoate: ndls. from dil. alc., m.p. 77–78° (2). [From ethyl *p*-hydroxybenzoate (1:1534) with SO_2Cl_2 (2); for use as disinfectant see (14).]

—— 3-Chloro-4-methoxybenzoic acid (3-chloroanisic acid): scales from dil. AcOH, m.p. 214–215° (16), 213° (4) (15), 212–214° (17). [Prepd. indirectly from 3-chloro-4-methoxybenzamide with HNO_2 (15), from 3-chloro-4-methoxytoluene by oxidn. with CrO_3/AcOH (16) or alk. $KMnO_4$ (17).]

—— 3-Chloro-4-hydroxybenzamide: ndls. from acetone + ether, m.p. 181–182° (3). [Prepd. indirectly from 3-chloro-4-hydroxybenzonitrile with dil. H_2SO_4 at 160° (3).]

3:4675 (1) Lossner, *J. prakt. Chem.* (2) **13**, 432–435 (1876). (2) Mazzara, *Gazz. chim. ital.* **29**, I 385–387 (1899). (3) Biltz, *Ber.* **37**, 4035–4036 (1904). (4) von Auwers, *Ber.* **30**, 1473–1474 (1897). (5) Hasse, *Ber.* **10**, 2192–2194 (1877). (6) Leulier, Pinet, *Bull. soc. chim.* (4) **41**, 1364–1365 (1927). (7) Tishchenko, *J. Russ. Phys.-Chem. Soc.* **60**, 153–162 (1928); *Cent.* **1928**, II 768; *C.A.* **22**, 3397 (1928). (8) Chem. Fabrik von Heyden, Ger. 69,116; *Friedländer* **3**, 847. (9) Coppadoro, *Gazz. chim. ital.* **32**, I 554 (1902). (10) Sabalitschka, *Arch. Pharm.* **267**, 675–685 (1929).
(11) Sabalitschk
20, 3060 (1926).
I 2670–2671; *C.A*
II 271. (14) Sabalitschka, Böhn, Ger. 592,826, Sept. 11, 1930; *Cent.* **1934**, I 3369. (15) Gattermann, *Ber.* **32**, 1118, 1121 (1899). (16) Schall, Dralle, *Ber.* **17**, 2529 (1884). (17) Peratoner, Vitale, *Gazz. chim. ital.* **28**, I 217 (1898).

3:4680 8-CHLORONAPHTHOIC ACID-1



$C_{11}H_7O_2Cl$ Beil. IX - 651
IX_1-(276)

M.P. **171–171.5°**	(1)
170–170.5°	(1)
169–170°	(2)
168–169°	(3)
167–168°	(3)
167°	(4) (5)

Cryst. from C_6H_6 (2), scales from alc. (4). — Subl. in ndls. (4).

[For prepn. of $\bar{C}$ from naphthalic acid (1:0890) via conv. with $Hg(OAc)_2$ to anhydro-8-hydroxymercuri-1-naphthoic acid and subsequent reactn. with Cl_2 in AcOH see (1) (3) (6) (7) cf. (8); from 8-aminonaphthoic acid-1 [Beil. XIV-534, XIV_1-(623)] via diazotization and reactn. with CuCN see (4); from α-naphthoic acid (1:0785) with Cl_2 in AcOH contg. I_2 see (4); from 8-nitronaphthoic acid-1 [Beil. IX-653] (3) with $SOCl_2$ in C_6H_6 (some dichloronaphthostyril also being formed) see (3); from 8-chloro-1-naphthonitrile (see below) by hydrolysis see (9); from 8-chloro-1-naphthoamide (see below) by hydrolysis with $AcOH/H_2SO_4$ + $NaNO_2$ see (5) (2).]

$\bar{C}$ with Cl_2 in AcOH contg. I_2 yields (4) (1) 5,8-dichloronaphthoic acid-1 [Beil. IX-651], scales from alc., m.p. 186–187° (4) (1).

$\bar{C}$ with PCl_5 yields (5) 8-chloro-1-naphthoyl chloride (props. not reported).

$\bar{C}$ with cold red fumg. HNO_3 yields (10) (11) 8-chloro-5-nitronaphthoic acid-1, lfts. or ndls. from alc., m.p. 227° (10), 225–226° (11). [This prod. with Cu bronze in boilg. toluene for 3 hrs. yields (11) 5-nitronaphthoic acid-1 [Beil. IX-652], m.p. 241–242°.

Salts. $Ca\bar{A}_2.2H_2O$; ndls. sol. in 42 pts. cold aq. (4).

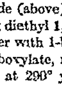
— Methyl 8-chloro-1-naphthoate: oil, b.p. 188–189° at 16.2 mm. (2). [From $\bar{C}$ with ethereal diazomethane (2).]

Ⓓ Ethyl 8-chloro-1-naphthoate: ndls. from alc., m.p. 50° (4), 49–50° (5). [From dry $Ag\bar{A}$ with EtI at 100° (4) or from acid chloride (above) with NaOEt (5).] [For reactn. of this ester with Cu bronze at 290° yielding diethyl 1,1′-binaphthyl-8,8-dicarboxylate, m.p. 183°, see (5) (9); for reactn. of the ester with 1-bromonaphthalene + Cu bronze at 290° yielding ethyl 1,1′-binaphthyl-8-carboxylate, m.p. 146°, see (9); for reactn. of this ester with 2-bromonaphthalene + Cu at 290° yielding ethyl 1,2′-binaphthyl-8-carboxylate, m.p. 105°, see (9).]

— 8-Chloro-1-naphthonitrile: ndls. from MeOH, m.p. 150–151° (9), 145–146° (2), b.p. 200° at 18 mm. (9), 242–244° at 15.5 mm. (7) (2). [From 8-chloronaphthylamine-1 [Beil. XII-1256] via diazotization and reactn. with CuCN (yields: 57% (5), 22% (2)) (9).]

— 8-Chloro-1-naphthoamide: ndls. from alc., m.p. 203.5° (5). [From the nitrile (above) by hydrolysis with $AcOH/H_2SO_4$ (5).]

3:4680 (1) Whitmore, Fox, *J. Am. Chem. Soc.* **51**, 3363–3367 (1929). (2) Bergmann, Hirshberg, *J. Chem. Soc.* **1936**, 334. (3) Rule, Barnett, *J. Chem. Soc.* **1932**, 175–179. (4) Eckstrand, *J. prakt. Chem.* (2) **38**, 150–151 (1888). (5) Kalb, *Ber.* **47**, 1725–1728 (1914). (6) Corbellini, Barbari, *Giorn. chim. ind. applicata* **15**, 335–337 (1933), *Cent.* **1933**, II 2818; *C.A.* **27**, 5737 (1933). (7) Corbellini, Ital. 332,963, May 19, 1934, *Cent.* **1937**, I 2460. (8) Leuck, Perkins, Whitmore, *J. Am. Chem. Soc.* **51**, 1831–1836 (1929). (9) Meisenheimer, Beisswenger, *Ber.* **65**, 32–42 (1932). (10) Eckstrand, *J. prakt. Chem.* (2) **38**, 253–254 (1888).
(11) Rule, Pursell, Brown, *J. Chem. Soc.* **1934**, 168–171.

3:4690 2,5-DICHLOROHYDROQUINONE (p-Dichlorohydroquinone)  $C_6H_4O_2Cl_2$ Beil. VI - 850
VI_1—
VI_2-(845)

M.P. 172° (1) (2)
170° (3)
166° (4)

[See also 2,5-dichlorobenzoquinone-1,4 (3:4470).]

Colorless ndls. from boilg. aq., tbls. from C_6H_6, moclinic pr. from acetone; spar. sol. cold aq., sol. boilg. aq., very eas. sol. alc., ether, or warm AcOH. — Sublimes in ndls.

[For prepn. of $\bar{C}$ from 2,5-dichlorobenzoquinone-1,4 (3:4470) by reductn. with SO_2 see (5); from chlorobenzoquinone-1,4 (3:1100) with hot conc. HCl (83% yield (6)) (4) or in $CHCl_3$ with HCl gas (4) see indic. refs.; from hydroquinone (1:1590) with HCl + $KClO_3$ (2) (7), in AcOH or better $CHCl_3$ with Cl_2 (poor yield together with 2,3-isomer) (6), or in MeOH with Cl_2 (8) see indic. refs.; from chlorohydroquinone (3:3130) with HCl + $KClO_3$ (68% yield) see (9), from 2,5-dichloro-*p*-aminophenol (10) by diazotization in H_2SO_4 + $ZnSO_4$ soln. and hydrolysis of the diazonium salt (10).]

[For use of $\bar{C}$ as an antioxidant and gum inhibitor in cracked gasoline see (11); for use in aq. petroleum emulsion as insecticidal oil spray see (12); for use as vulcanization accelerator see (19).]

$\bar{C}$ on oxidn. with $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ + dil. H_2SO_4 (7) (2) (9) (13) (14) or even with conc. HNO_3 at ord. temp. (4) yields 2,5-dichlorobenzoquinone-1,4 (3:4470) q.v. — [For studies of oxidn.-reductn. potential of system $\bar{C}$ + corresp. quinone see (9) (15) (16).]

Ⓓ 2,5-Dichlorohydroquinone diacetate: colorless ndls. from dil. alc., m.p. 141° (4) (17). [From $\bar{C}$ with Ac_2O (4) or from 2,5-dichlorobenzoquinone-1,4 (3:4470) in Ac_2O + AcOH with Zn dust (17).]

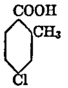
Ⓓ 2,5-Dichlorohydroquinone dibenzoate: colorless wooly ndls. from CS_2, m.p. 185° (4). [From $\bar{C}$ on refluxing with BzCl (4).]

Ⓓ 2,5-Dichlorohydroquinone dimethyl ether: colorless ndls., m.p. 126° u.c. (17), 125–127° (6), b.p. 261–263° u.c. at 744 mm. (16). [From $\bar{C}$ in dil. aq. NaOH on shaking with Me_2SO_4 (63% yield (6)), or from hydroquinone dimethyl ether in AcOH with Cl_2 (17) (18).] [This prod. with fumg. HNO_3 in cold does *not* nitrate but oxidizes to 2,5-dichlorobenzoquinone-1,4 (3:4470) (17).]

3:4690 (1) Krafft, *Ber.* **10**, 800 (1877). (2) Ling, *J. Chem. Soc.* **61**, 558 (1892). (3) Fels, *Z. Krist.* **37**, 481 (1903). (4) Levy, Schultz, *Ann.* **210**, 148–150 (1881). (5) Städler, *Ann.* **69**, 312–318 (1849). (6) Eckert, Endler, *J. prakt. Chem.* (2) **104**, 83–84 (1922). (7) Hammick, Hampson, Jenkins, *J. Chem. Soc.* **1938**, 1264. (8) Plazek, *Roczniki Chem.* **10**, 761–776 (1930); *Cent.* **1931**, I 1428; *C.A.* **25**, 1504 (1931). (9) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2205–2206 (1923). (10) Skraup, Steinruck (to Rheinische Kamfer-Fabrik), Ger. 431,513, July 10, 1926; *Cent.* **1926**, II 1462.

(11) Clarke, Towne (to Texas Co.), U.S. 2,023,871, Dec. 10, 1935; *Cent.* **1936**, I 2671; *C.A.* **30**, 851 (1936). (12) Yates (to Shell Development Co.), U.S. 1,778,240, Oct. 14, 1930; *Cent.* **1931**, I 2799; *C.A.* **24**, 5928 (1930). (13) Kehrmann, Grab, *Ann.* **303**, 12–14 (1898). (14) Hantzsch, Schniter, *Ber.* **20**, 2279–2282 (1887). (15) Hunter, Kvalnes, *J. Am. Chem. Soc.* **54**, 2874–2875, 2878 (1932). (16) Kvalnes, *J. Am. Chem. Soc.* **56**, 667–670 (1934). (17) Kohn, Gurewitsch, *Monatsh.* **56**, 135–136 (1930). (18) Habermann, *Ber.* **11**, 1034–1035 (1878). (19) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, II 3134.

3:4700 4-CHLORO-2-METHYLBENZOIC ACID



$C_8H_7O_2Cl$ Beil. IX-468 IX_1—

M.P.	172°	(1)
	171–172°	(10)
	171°	(2)
	170° u.c.	(3) (8)
	169–170°	(4)
	169°	(5)
	166–168°	(6)
	166°	(7)

Colorless ndls. from aq. alc., dil. AcOH or C_6H_6; eas. sol. hot aq.; eas. volatile with steam.

[For prepn. of $\bar{C}$ from 4-chloro-1,2-dimethylbenzene (3:8675) by oxidn. with boilg. dil. HNO_3 (D = 1.20) (7) or with 20 pts. dil. HNO_3 (D = 1.10) in s.t. at 160° for 5–6 hrs. (8) (by this method $\bar{C}$ is always accompanied by the isomeric 5-chloro-2-methylbenzoic acid (3:4670) separable by its less sol. calcium salt (1) (8) (7)) see indic. refs.; from 4-chloro-2-methylbenzaldehyde [Beil. VII-296] by air oxidn. see (4); from chloromethyl 4-chloro-2-methylphenyl ketone (*4-chloro-2-methylphenacyl chloride*) [Beil. VII-306] by oxidn. with $KMnO_4$ see (2); from β-chloroethyl 4-chloro-2-methylphenyl ketone (5) by oxidn. at 100° with mixt. of equal pts. conc. HNO_3 and aq. see (5); from 4-chloro-2-methylbiphenyl (3) by oxidn. with CrO_3/AcOH (8% yield) see (3); from 1-methyl-1-(trichloromethyl)cyclohexadiene-2,5-one-4 [Beil. VII-149] by treatment with PCl_5 giving 4-chloro-2-methylbenzotrichloride, followed by alk. hydrolysis of the latter, see (9); from 4-chloro-2-methylbenzonitrile, m.p. 67° (1) (10), by boilg. for 16 hrs. with 8% aq. KOH see (1) (10).]

$\bar{C}$ on oxidn. with alk. $KMnO_4$ (7) or with 10–20 pts. dil. HNO_3 ($D = 1.13$) in s.t. at 180–200° for 5 hrs. (1) yields 4-chlorophthalic acid (3:4390).

$\bar{C}$ fused with KOH yields (7) 4-hydroxy-2-methylbenzoic acid [Beil. X-215], m.p. 172–173° (7).

Salts. $NH_4\bar{A}$, eas. sol. aq.; $K\bar{A}.H_2O$, very eas. sol. aq.; $Ca\bar{A}_2.3H_2O$ more sol. in aq. than corresp. salt of 5-chloro-2-methylbenzoic acid (3:4670); $Ba\bar{A}_2.4H_2O$, more eas. sol. aq. than calcium salt (for details see (1)).

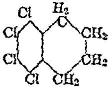
—— Methyl 4-chloro-2-methylbenzoate: unrecorded.

—— Ethyl 4-chloro-2-methylbenzoate: oil, b.p. 258° (1), $D_4^{20} = 1.1626$ (10), $n_{He}^{20} = 1.52705$ (10) [From $\bar{C}$ in EtOH with HCl gas (1) or from the amide (see below) with ethyl nitrite in s.t. at 140° for 4–5 hrs. (1).]

—— 4-Chloro-2-methylbenzamide: colorless ndls. from hot aq., from alc. or ether, m.p. 183° (1). [Obtd. indirectly by partial sapon. of corresp. nitrile (above) (1).]

3:4700 (1) Claus, Stapelberg, *Ann.* **274**, 287–291 (1893). (2) Kunckell, *Ber* **41**, 2648 (1908). (3) Huntress, Seikel, *J. Am. Chem. Soc.* **61**, 820 (1939). (4) von Auwers, Keil, *Ber.* **38**, 1696 (1905). (5) Mayer, Müller, *Ber.* **60**, 2281 (1927). (6) Mayer, Albert, Schon, *Ber.* **65**, 1295–1299 (1932). (7) Krüger, *Ber.* **18**, 1757 (1885). (8) Claus, Bayer, *Ann.* **274**, 308 (1893). (9) von Auwers, Jülicher, *Ber.* **55**, 2167–2168, 2179–2180 (1922). (10) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 15–16, 18 (1929).

3:4703 5,6,7,8-TETRACHLORO-1,2,3,4-TETRAHYDRONAPHTHALENE (5,6,7,8-Tetrachlorotetralin)



$C_{10}H_8Cl_4$ Beil. V — V_1— V_2-(386)

M.P. 172° (1)
174° (2)

B.P. 180° at 26 mm. (1)

[*See also naphthalene tetrachloride* (3:4750).]

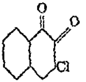
Cryst. from AcOH.

[For prepn. of $\bar{C}$ from 1,2,3,4-tetrahydronaphthalene (tetralin) (1:7550) with Cl_2 in pres. of I_2 (15% yield (2)) at 15° in diffuse daylight see (1) (2); for formn. in small amt. from tetralin during prepn. of 7-chloro-1,2,3,4-tetrahydronaphthalene (β-chlorotetralin) with Cl_2 in pres. of I_2 at 10° see (1).]

$\bar{C}$ with $2Br_2$ in boilg. CS_2 yields (1) 1,2-dibromo-5,6,7,8-tetrachloronaphthalene [Beil. V_2-(388)], m.p. 142° (1), which with alc. (?) NaOEt gives (alm. quant. yield (1)) 1,2,3,4-tetrachloronaphthalene [Beil. V_2-(446)], m.p. 198°

3:4703 (1) von Braun, *Ber* **56**, 2337 (1923). (2) Wynne, *J. Chem. Soc.* **1946**, 61.

3:4704 3-CHLORONAPHTHOQUINONE-1,2 (3-Chloro-β-naphthoquinone)



$C_{10}H_5O_2Cl$ Beil. VII-720 VII_1—

M.P. 172° (1) (2) (3)

Red ndls. from $CHCl_3$. — Sol. hot alc., AcOH, C_6H_6, $CHCl_3$.

[For prepn. of $\bar{C}$ from β-naphthol (1:1540) by conversion with Cl_2 in AcOH (2) to 1,1,3,4-tetrachloro-2-keto-1,2,3,4-tetrahydronaphthalene [Beil. VII-371] (lfts. of monohydrate from aq., m.p. 90–91°; anhydrous lfts. or ndls. from hot lgr., m.p. 101–103°)

followed by treatment with aq. Na_2CO_3 (2) (3) (overall yield of C̄ is 50% (4)). — For prepn. of C̄ from naphthoquinone-1,2 (1:9002) with Cl_2 in AcOH (1) (5), or from 1,3-dichloronaphthol-2 (3:1090) by oxidn. with conc. HNO_3 in AcOH (3), see indic. refs.]

C̄ on reduction with SO_2 in AcOH gives (1) 3-chloro-1,2-dihydroxynaphthalene [Beil. VI-975], colorless ndls., m.p. 116–117° (1).

[C̄ on oxidn. with aq. $Ca(OCl)_2$ undergoes rupture of the quinoid ring and a subsequent series of changes (5) resulting in formation of (phthalidyl-3)-dichloroacetic acid [Beil. XVIII-419], tbls. of monohydrate from aq., anhydrous ndls. from C_6H_6, m.p. 157°, accompanied by some 2,2-dichloroindandione-1,3 [Beil. VII-696, VII_1-(375)], m.p. 124–125°.]

[C̄ although insol. in aq. Na_2CO_3 gradually dissolves in dil. aq. alkali with conversion (1) to 3-chloro-2-hydroxy-naphthoquinone-1,4 (3-chloro-4-hydroxynaphthoquinone-1,2) [Beil. VIII-304], yel. ndls. from alc., m.p. 215°.]

[C̄ with alc. NH_3 on htg. gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-imine-4 (3-chloro-4-aminonaphthoquinone-1,2) [Beil. VIII-305], m.p. abt. 260°.]

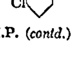
[C̄ with alc. aniline on htg. similarly gives (1) 3-chloro-2-hydroxynaphthoquinone-1,4-anil-4 (3-chloro-4-anilino-naphthoquinone-1,2) [Beil. XII-225], yel. ndls. from AcOH, m.p. 253°.]

C̄ with 2,3,-dimethylbutadiene-1,3 (1:8050) in spec. purified $CHCl_3$ in s.t. at 100° in dark for 1 hr. readily forms (70% yield (4)) a Diels-Alder type adduct $C_{16}H_{15}O_2Cl$, lemon-yel. ndls. from ether/pet. ether, m.p. 87–88°; this adduct is unstable even at 10° and in alc. or ether soln. on shaking with air loses HCl and is oxidized (by loss of 2 hydrogen atoms) giving (87% yield (4)) 2,3,-dimethylphenanthraquinone, m.p. 237–238° u.c., 242–243° cor. (4). — For study of reaction of C̄ with excess 2,3-dimethylbutadiene-1,3 (1:8050) giving 36% yield of a halogen-free prod. of m.p. 135° see (6).

—— **3-Chloronaphthoquinone-1,2-oxime-1 (3-chloro-1-nitrosonaphthol-2)** [Beil. VII-721]: yel.-red ndls. from hot alc., m.p. 167–168° dec. (7). [Prepd. indirectly.]

3:4704 (1) Zincke, *Ber.* **19**, 2497 (1886). (2) Zincke, Kegel, *Ber.* **21**, 3550–3552 (1888). (3) Zincke, Kegel, *Ber.* **21**, 3380, 3386 (1888). (4) Fieser, Dunn, *J. Am. Chem. Soc.* **59**, 1019–1020 (1937). (5) Zincke, Schmidt, *Ber.* **27**, 737–739 (1894). (6) Fieser, Dunn, *J. Am. Chem. Soc.* **59**, 1021–1024 (1937). (7) Zincke, Schmunk, *Ann.* **257**, 140–145 (1890).

3:4705 5-CHLORO-2-HYDROXYBENZOIC ACID (5-Chlorosalicylic acid) $C_7H_5O_3Cl$ Beil. X - 102, X_1-(47)



M.P. [170°	(1)]	M.P. (*contd.*) 171–172.5°	(10)
173°	(2)	170–171°	(11)
172.5°	(3)	168°	(12) (13)
172–173°	(4)	167.5°	(14) (15) (16)
172°	(5) (6) (7) (8) (9) (22) (27)	167–168°	(17) (18) (19)

Colorless ndls. from aq. or alc.; sol. in 1100 pts. aq. at 20° and in 80 pts. aq. at 100° (17); eas. sol. alc., ether, C_6H_6, $CHCl_3$, AcOH; spar. sol. lgr. — Volatile with steam (12). — Shows sternutatory props.

[For prepn. of C̄ from *p*-chlorophenol (3:0475) in CCl_4 with aq. NaOH (very small yield (15)) in pres. of Cu (19) or in CCl_4 with alc. KOH in s.t. at 140° for 5–6 hrs. (17) see indic. refs.; from dry sodium *p*-chlorophenolate with CO_2 at 140–150° under press. see (12) (20); from salicylic acid (1:0780) with Cl_2 in CS_2 (65% yield (38)) (3), in MeOH (21) or EtOH (22) (much 3,5-dichlorosalicylic acid (3:4035) also being formed), in AcOH (85%

yield (4)) or in nitrobenzene at 50–60° (23), or with $C_6H_5ICl_2$ in suitable solvents (89% yield (2)), or by htg. with $SbCl_5$ (14), or with HCl + 30% H_2O_2 (56–66% yield (6)), see indic. refs.; from mono K salicylate in aq. with Cl_2 (24) or from di-potassium salicylate with KOCl (1) (much 3,5-dichlorosalicylic acid (3:4935) being also formed) see indic. refs.]

[For prepn. of $\bar{C}$ from 5-chloro-2-aminobenzoic acid (5-chloroanthranilic acid) [Beil. XIV-365] with nitrous acid at 50° see (11); from 5-amino-2-hydroxybenzoic acid (5-aminosalicylic acid) [Beil. XIV-579, XIV_1-(650)] via diazotization and use of Cu_2Cl_2 reactn. (62–71% yield (16)) (25) see indic. refs.; from 5-chloro-2-hydroxybenzonitrile [Beil. X-104] by hydrolysis with H_2SO_4 see (13); from ethyl 5-chloro-2-hydroxybenzoate (see below) by hydrolysis with KOH see (7) (25), from 5-chloro-2-methoxybenzoic acid (see below) by cleavage with conc. HI see (10); from chloral-5-chlorosalicylamide (see below) by hydrolysis with 10% NaOH see (26); from 5-chlorosalicylin by oxidn. with $K_2Cr_2O_7$ + H_2SO_4 (18) or with $KMnO_4$ followed by acid hydrolysis (9) see indic. refs ; from 6-chloro-2,3-dimethylchromone (27), 6-chloro-2,3-diphenylchromone (28), or 7-chloro-1,2,3,4-tetrahydroxanthone (5) by alk. hydrol. see indic. refs.]

[For use of various esters of $\bar{C}$ as mothproofing agents (29), as insecticides (30), or as plasticizers (31) (32) see indic. refs.; for studies of bactericidal power of $\bar{C}$ see (33) (34); for study of fate of $\bar{C}$ in animal body see (35)]

[$\bar{C}$ on electrolytic reduction in aq. alc. H_2SO_4 yields (36) 5-chloro-2-hydroxybenzyl alcohol [Beil. VI-893], m.p. 93° (36); $\bar{C}$ on reductn. with Na/Hg as directed (16) yields 5-chloro-2-hydroxybenzaldehyde (3:2800).]

[$\bar{C}$ with PCl_5 (37) in lgr. (38) yields 4-chloro-2-chloroformylphenylphosphoryl dichloride, $Cl.CO.C_6H_3Cl.O\text{-}P(O)Cl_2$ [Beil. X-103], oil, b.p. 183–184° at 13 mm. (38); $\bar{C}$ with PCl_3 yields (38) 4-chloro-2-chloroformylphenyl metaphosphite, $Cl.CO.C_6H_3Cl.O\text{-}P{:}O$ [Beil. X-103], m.p. abt. 55–57°, b.p. 155–156° at 14 mm. (38).]

[$\bar{C}$ with $ClSO_3H$ at 50–70° yields (39) 3-chlorosulfonyl-5-chloro-2-hydroxybenzoic acid [Beil. XI_1-(106)], pr. from AcOH, m.p. 206–207° (39).]

[$\bar{C}$ with HNO_3 + conc. H_2SO_4 at 0° (23), or $\bar{C}$ on warming with fumg. HNO_3 (22), or $\bar{C}$ in AcOH treated with 5 pts. fumg. HNO_3 in AcOH (40), yields 5-chloro-3-nitrosalicylic acid [Beil. X-120], pale yel. ndls , m.p. 162–163° (22); note that by loss of CO_2 and further nitration 4-chloro-2,6-dinitrophenol [Beil. VI-260, VI_1-(128)], yel. ndls. from aq., m.p. 80° (22), is also formed.]

[$\bar{C}$ in alc. with I_2 + HgO gives (41) 5-chloro-x-iodo-salicylic acid, colorless ndls. from hot dil. alc , m.p. 224° sl. dec. (41); $\bar{C}$ in alk. with I_2/KI yields (25) by loss of CO_2 and further iodination 4-chloro-2,6-diiodophenol [Beil. VI_1-(112)], yellowish ndls. from alc., m.p. 108° (25) (ethyl ether, m.p. 69°, acetate, m.p. 127.5° (25)).]

$\bar{C}$ in aq. soln. gives with $FeCl_3$ a violet coloration.

Salts. $Li\bar{A}, 2H_2O$ (8); $Na\bar{A}$ (8) (12), $K\bar{A}$ (8) all eas. sol. aq ; $Ca\bar{A}_2.3H_2O$ (14), $Ba\bar{A}_2\,3H_2O$ (11) (12) (14) (17) (18) see indic. refs.; $Pb\bar{A}_2$ (11), $Ag\bar{A}$ (12) (18), insol. aq.

Ⓓ **Methyl 5-chloro-2-hydroxybenzoate** (methyl 5-chlorosalicylate): ndls. from alc., m.p. 50° (1), 48° (7) (12), b p. 249° sl. dec. (12). [From $\bar{C}$ in MeOH with HCl gas (12), or from $Ag\bar{A}$ with MeI (1): also from methyl salicylate (1:1750) by chlorination with methyl *N,N*-dichlorocarbamate in AcOH (44).]

—— **Ethyl 5-chloro-2-hydroxybenzoate** (ethyl 5-chlorosalicylate): ndls. from alc , m.p. 25° (7). [From ethyl salicylate (1:1755) with SO_2Cl_2 (7).]

Ⓓ **5-Chloro-2-methoxybenzoic acid**: ndls. from aq., m.p. 82° (42), 81–82° (10), 80–81° (4). [Obtd. indirectly from 2-methoxybenzoic acid (1:0685) in AcOH with Cl_2 (4), or from 5-chloro-2-methoxybenzonitrile by alk. hydrolysis (43).]

Ⓓ **5-Chloro-2-ethoxybenzoic acid:** lfts. from dil. alc., m.p. 118° (7).

Ⓓ **5-Chloro-2-acetoxybenzoic acid:** cryst. from C_6H_6, m.p. 149° (8), 148° (42), 142° (25). [From $\bar{C}$ with AcCl (42).]

Ⓓ **5-Chloro-2-hydroxybenzamide:** lfts. from alc. or C_6H_6, m.p. 226–227° (26) (13), 223.5–224° (7), 222–223° (8). [From methyl or ethyl 5-chlorosalicylates (above) with alc. NH_3 (7).] [This amide with chloral (3:5210) gives on warming (26) chloral-5-chloro-2-hydroxybenzamide, ndls. from C_6H_6, m.p. 148–149° dec. (26).]

3:4705 (1) Lassar-Cohn, Schultze, *Ber.* **38**, 3800 (1905). (2) Neu, *Ber.* **72**, 1511 (1939). (3) Hübner, Brenken, *Ber.* **6**, 174 (1873). (4) Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci.* A-8, 211–212 (1938). (5) Hall, Plant, *J. Chem. Soc* **1933**, 234. (6) Leulier, Pinet, *Bull. soc. chim.* (4) **41**, 1363 (1927). (7) Mazzara, *Gazz. chim. ital.* **29**, I 340–347 (1899). (8) Smith, *Ber.* **11**, 1226–1227 (1878). (9) van Wawern, *Arch. Pharm.* **235**, 567–568 (1897). (10) Peratoner, Condorelli, *Gazz. chim. ital.* **28**, I 211–212 (1898).

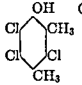
(11) Hübner, Weiss, *Ber.* **6**, 175 (1873). (12) Varnholt, *J. prakt. Chem.* (2) **36**, 19–22 (1887). (13) Biltz, Stepf, *Ber.* **37**, 4026–4027 (1904). (14) Beilstein, *Ber.* **8**, 816 (1875); *Ann.* **179**, 285 Note 2 (1875). (15) Sen, Ray, *J. Indian Chem. Soc.* **9**, 176 (1932). (16) Weil, Traun, Marcel, *Ber.* **55**, 2664–2665 (1922). (17) Hasse, *Ber.* **10**, 2190–2192 (1877). (18) Visser, *Arch. Pharm.* **235**, 549–550 (1897). (19) Zeitner, Landau, Ger 258,887, April 17, 1913; *Cent.* **1913**, I 1641–1642. (20) Chem. Fabrik von Heyden, Ger. 33,635, May 10, 1885, *Friedländer* **1**, 234 (1877/87).

(21) Plazek, *Roczniki Chem* **10**, 761–776 (1930); *Cent.* **1931**, I 1428; *C.A.* **25**, 1504 (1931). (22) Smith, Peirce, *Am. Chem. J.* **1**, 176–181 (1879/80); *Ber.* **13**, 34–36 (1880). (23) B.A.S.F., Ger. 137,118, Nov. 20, 1902, *Cent.* **1902**, II 1439–1440. (24) Cahours, *Ann. chim.* (3) **13**, 108–111 (1845); *Ann.* **52**, 341–342 (1844). (25) Brennans, Girod, *Compt. rend.* **186**, 1553–1555 (1928). (26) Hirwe, Rana, *Ber.* **72**, 1351–1352 (1939). (27) Simonis, Schuhmann, *Ber.* **50**, 1144–1145 (1917). (28) Wittig, *Ann.* **446**, 190 (1925). (29) I.G., Brit. 274,425, Sept. 7, 1927; French 635,973, March 29, 1928; *Cent.* **1929**, I 434. (30) I G , French 702,768, April 16, 1931; *Cent.* **1931**, II 3530; Austrian 125,712, Dec. 10, 1931; *Cent.* **1932**, I 2886.

(31) Grether, DuVall (to Dow Chem. Co.), U.S. 2,198,583, April 23, 1940; *C.A.* **34**, 5965 (1940). (32) Grether, DuVall (to Dow Chem. Co.), U.S. 2,234,374, March 11, 1941; *C.A.* **35**, 3738 (1941). (33) Delauney, *J. pharm. chim.* (8) **25**, 254–266, 545–560 (
1938, I 2019. (34) Rochaix, Pinet, *Bull. sci. pharmacol.* **34**,
C.A. **22**, 443 (1928). (35) Girod, *J. pharm. chim.* (8) **9**, 5
C.A. **24**, 163 (1930). (36) Mettler, *Ber.* **39**, 2939 (1906).
Ger. 89,556; *Friedländer*, **4**, 156. (38) Anschütz, Anspac
Bayer and Co., Ger. 264,786, Sept. 23, 1913; *Cent.* **1913**, II 1350. (40) Ref. 38, pp. 338–339.

(41) Smith, Knerr, *Am. Chem. J.* **8**, 95–96 (1886) (42) Anschütz, *Ann.* **367**, 263 (1909). (43) Brand, Pabst, *J. prakt Chem.* (2) **120**, 207–208 (1928). (44) Bougault, Chabrier, *Compt. rend.* **213**, 400–402 (1941); Chabrier de la Saulniere, *Ann. chim.* (11) **17**, 353–370 (1942); *C.A.* **38**, 3255 (1944).

3:4707 3,5,6-TRICHLORO-2,4-DIMETHYLPHENOL (Trichloro-*m*-4-xylenol)



$C_8H_7OCl_3$ Beil. VI — VI_1— VI_2-(460)

M.P. 174° (1)

Pale yellowish ndls.

[For prepn. of $\bar{C}$ from 3,5,6-trichloro-2,4-dimethylaniline (1) via diazotization and hydrolysis (yield not stated) see (1).]

[For prepn. of basic Hg and Bi derivs. see (1).]

Ⓓ **3,5,6-Trichloro-2,4-dimethylphenol methyl ether:** m.p. 91.5° (1). [From $\bar{C}$ with Me_2SO_4 + aq alk. (1).]

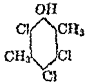
Ⓓ **3,5,6-Trichloro-2,4-dimethylphenol ethyl ether:** m.p. 53.5° (1).

Ⓓ **3,5,6-Trichloro-2,4-dimethylphenyl acetate:** m.p. 86° (1).

—— **3,5,6-Trichloro-2,4-dimethylphenyl benzoate:** unreported.

3:4707 (1) Bures, Borgmann, *Časopis Českoslov Lékárnictva*, **7**, 270–280 (1927); *Cent.* **1928** I 1171; *C.A.* **22**, 4503 (1928).

3:4709 3,4,6-TRICHLORO-2,5-DIMETHYLPHENOL (*Trichloro-p-xylenol*)



$C_8H_7OCl_3$ Beil. VI — VI_1— VI_2-(467)

M.P. 175° (1)

Pale greenish ndls from alc, AcOH, or pet eth or by sublimation — Readily sol. in ether, C_6H_6, or $CHCl_3$, less sol alc or other org solvents; insol aq — Volatile with steam.

[For prepn. of $\bar{C}$ from 3,4,6-trichloro-2,5-dimethylaniline (1), via diazotization and *hydrolysis (yield not stated), see (1).*]

[For conversion of $\bar{C}$ to basic Hg or Bi derivs. see (1)]

Ⓓ **3,4,6-Trichloro-2,5-dimethylphenol methyl ether:** yellowish ndls from dil. alc. or pet ether, m p 91° (1) [From $\bar{C}$ with Me_2SO_4 + hot aq. alk (1)]

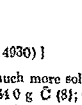
Ⓓ **3,4,6-Trichloro-2,5-dimethylphenol ethyl ether:** alm colorless cryst, m p. 79° (1) [From $\bar{C}$ with Et_2SO_4 + hot aq. alk. (1).]

Ⓓ **3,4,6-Trichloro-2,5-dimethylphenyl acetate:** pr. from alc + ether, m.p. 103° (1). [From $\bar{C}$ with Ac_2O *(10 pts.) + trace of H_2SO_4 on htg (1).*]

Ⓓ **3,4,6-Trichloro-2,5-dimethylphenyl benzoate:** hexag pr from alc. or pet. ether, *m.p. 101° (1) [From $\bar{C}$ with* benzoyl *chloride* + aq alk. (1).]

3:4709 (1) Bures, Rubes, *Collection Czechoslov Chem. Commun.* **1**, 648–657 (1929), *C.A.* **24**, 1851 (1930) also in *Časopis Českoslov Lékárnictva*, **8**, 225–231, 258–264 (1928); *Cent.* **1929**, I 506–507; *C.A* **23**, 3674 (1929).

3:4711 *d,l*-α,α′-DICHLOROSUCCINIC ACID (*allo*-Dichlorosuccinic acid; isodichlorosuccinic acid)



$C_4H_4O_4Cl_2$ Beil. II - 619 II_1-(267) II_2-(557)

M.P.	*175° u.c.*	(1) (2) (3) (4) (12)
	174–175° dec.	(5) (6)
	173°	(7) (8)
	170–172° cor., dec.	(9)
	170° dec.	(10)

[*See also meso-α,α′-dichlorosuccinic acid* (3.4930)]

Cryst. from ether + pet ether. — $\bar{C}$ is much more sol. aq. than its *meso* stereoisomer; e.g., 100 cc. satd aq. soln. of $\bar{C}$ at 0° conts 54 0 g $\bar{C}$ (8); $\bar{C}$ is eas. sol. ether, less so in ...

[*For prepn. of $\bar{C}$ from disodium salt of fumaric acid* (1:0895) with ... in dark or diffuse daylight at 5° (yields: 75% (7) ... (note that as a side reactn some addn. o ... 10% (9) chloromalic acid, and that under some (ca ... the reactn. yields as much as 80% (9) of the *meso* stereoisomer (3.4... from maleic anhydride (1:0625) in CCl_4 by addn. of Cl_2 *in sunlight followed by hydrolysis* see (12) (9); from *d,l*-α,α′-diaminosuccinic acid [Beil. IV-487, IV_2-(901)] in aq. HCl soln with NOCl see (2); *from benzoquinone*

dichloride [Beil. VII-573] (13) or toluquinone dichloride [Beil. VII-576] (13) by oxidn. with aq. $KMnO_4$ (or $BaMnO_4$) at 0° see (3); from *d,l*-α,α′-dichlorosuccinyl (di)chloride (3:0395) by aq. hydrolysis see (14)]

C̄ behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — For study of acid strength ($K_1 = 372.0 \times 10^{-4}$ at 16°; $K_2 = 18.0 \times 10^{-4}$ at 16.7° (8) cf. (15); for study of conductivity see (4).

[Salts (of metals): $(NH_4)_2\bar{A}.2H_2O$ (10), $K_2\bar{A}.H_2O$ (6), $KH\bar{A}.2H_2O$ (6), $CaA.2\frac{1}{2}H_2O$ (10), $Ba\bar{A}.7H_2O$ (10), $Cu\bar{A}.2\frac{1}{2}H_2O$ (10), all eas. sol. aq.; $Sr\bar{A}.7H_2O$ (10), sol. in 15 pts. aq.; $Pb\bar{A}.3H_2O$ (10) spar. sol. aq.]

C̄ on boilg. with aq. (12) or with aq. KOH (7) (6) or aq. acid (6) loses 1 HCl yielding chlorofumaric acid (3:4853); for study of rate at 25° see (7) (16).

[$K_2\bar{A}$ in aq. soln. maintained at neutrality at 100° yields mainly (6) *d,l*-tartaric acid (1:0550)]

C̄ with PCl_5 (2 moles) gives (100% yield (14)) *d,l*-α,α′-dichlorosuccinyl (di)chloride (3:0395), m p. 39°.

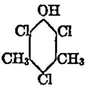
Ⓓ Dimethyl *d,l*-α,α′-dichlorosuccinate: m.p. 43° (see 3:0485).

—— Diethyl *d,l*-α,α′-dichlorosuccinate: oil (see 3:9578).

—— Acid salt of C̄ with *d,l*-α-phenylethylamine: pr. from aq., m.p. 149–150°, rap. htg. (6); satd. aq. soln. at 25° conts. 18.67 g./liter (6). [For details of resolution of C̄ with opt. act. α-phenylethylamine see (6) (1); note incidentally that, although m p. of C̄ is 175°, the m.p. of each of the opt. act. stereoisomeric forms is lower, viz., 166–167° dec. (6), 168° (1).]

(1892). (14) Lutz, *J. Am. Chem. Soc.* **49**, 1110 (1927). (15) Holmberg, *J. prakt. Chem.* (2) **84**, 164–165 (1911). (16) Holmberg, *Z. physik. Chem.* **79**, 165–167 (1912).

3:4713 2,4,6-TRICHLORO-3,5-DIMETHYLPHENOL (Trichloro-*m*-5-xylenol) $C_8H_7OCl_3$ Beil. S.N. 529



M.P. 177–178° (1)
175–177° (2) (4)

Yellow ndls. from lt. pet.

[For prepn of C̄ from 3,5-dimethylphenol (*m*-5-xylenol) (1:1455) with Cl_2 in hot CCl_4 (87% yield (1)) or by action of $ClSO_3H$ + conc. HCl + H_2O_2 (2) see indic. refs.; for formn. of C̄ from 3,5-dimethylphenol-2,4-*bis*-(sulfonyl chloride) (2) by preliminary KOH hydrolysis followed by action of conc. HCl + 30% H_2O_2 see (2) cf. (4).]

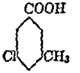
C̄ with fumg. HNO_3 is oxidized (64% yield (1)) to 2,6-dichloro-3,5-dimethylbenzoquinone-1,4 (3,5-dichloro-*m*-xyloquinone), yel. lfts, m.p. 177–178° (1), 178° u.c. (3).

[C̄ with $NaNO_2$ in AcOH at room temp. gives (48% yield (1)) of a mol. cpd. contg. 2 moles C̄ + 1 mole of 2,6-dichloro-3,5-dimethylbenzoquinone-1,4 (above), crimson cubes

from CCl_4, becoming yellow at 118–119° without melting, but fusing slowly from 133–164° (1).]

3:4713 (1) Raiford, Kaiser, *J. Org. Chem.* **4**, 565, 567 (1939). (2) Katscher, Lehr, *Monatsh.* **64**, 239–240 (1934). (3) Claus, Runschke, *J. prakt. Chem* (2) **42**, 124 (1890). (4) Lehr, *Anilin Farben-Ind. (Russ.)* **4**, 77–84 (1934); *Cent.* **1935**, I 1365, not in *C.A.*

3:4715 5-CHLORO-3-METHYLBENZOIC ACID $C_8H_7O_2Cl$ Beil. IX-479 IX_1—



M.P. 178° (1)

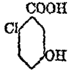
Ndls from dil alc.

[For formn. of Č (in very small yield) from 5-chloro-1,3-dimethylcyclohexadiene-3,5 (5-chloro-1,2-dihydro-*m*-xylene) [Beil. V-119, V_1-(64)] by oxidn. with boilg. 30% HNO_3 see (1).]

Č on oxidn. with $KMnO_4$ gives (1) 5-chlorobenzenedicarboxylic acid-1,3 (5-chloroisophthalic acid) (3:4960), m p. 278° (1), together with a little 5-hydroxybenzenedicarboxylic acid-1,3 (5-hydroxyisophthalic acid) [Beil. X-504, X_1-(257)], m.p. 288°.

3:4715 (1) Klages, Knoevenagel, *Ber.* **28**, 2045–2046 (1895).

3:4720 6-CHLORO-3-HYDROXYBENZOIC ACID $C_7H_5O_3Cl$ Beil. X-143 X_1—



M.P. 178–179° (1)
178° (2) (6)
177–178° (3)
176–177° (3)
175° (4)
169–170° (5)

Colorless cryst. from aq. [Ioniz. const. of Č at 25° = 1.40×10^{-3} (6)].

[For prepn. of Č from 6-chloro-3-aminobenzoic acid [Beil. XIV-412, XIV_1-(563)] via diazotization and boilg with aq. (yield: 60–70% (4) 10% (3)) see indic. refs.; from 6-amino-3-hydroxybenzoic acid [Beil XIV-591] via diazotization and use of Cu_2Cl_2 (?) see (1); from 6-chloro-3-hydroxytoluene (3:1535) via conv. with $POCl_3$ to 4-chloro-3-methylphenylphosphoric acid, oxidn. with $KMnO_4$ to 4-chloro-3-carboxyphenylphosphoric acid, and finally acid hydrolysis to Č see (3); for formn. of Č from methyl ether of Č (see below) by cleavage with HI see (5), from ethyl ester of Č (see below) by hydrolysis with 35% KOH see (2); from *m*-hydroxybenzoic acid (1:0825) with Cl_2 in MeOH (7) or in AcOH (1) see indic. refs.]

[Č on distn. with $Ba(OH)_2$ yields (5) *p*-chlorophenol (3:0475).]

[Č with cinnamic acid (1:0735) in conc. H_2SO_4 + a few drops fumg. H_2SO_4 (18% SO_3) gives (29% yield (3)) anthracoumarin, golden-yel. ndls. from AcOH or by sublimation, m.p. 274° (3).]

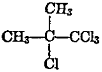
① Methyl 6-chloro-3-hydroxybenzoate: tbls. from dil. alc., m p. 100° (2). [From Č in MeOH with conc. H_2SO_4 (2).]

—— Ethyl 6-chloro-3-hydroxybenzoate: not specifically characterized. [For formn. (together with the isomeric ethyl 2-chloro-3-hydroxybenzoate) from ethyl *m*-hydroxybenzoate (1:1471) by actn. of SO_2Cl_2 see (2).]

—— 6-Chloro-3-methoxybenzoic acid: ndls. from AcOH, m.p. 173.5° (9), 170–171° (2) (8). [Prepd indirectly from methyl ester (above) with MeI + MeOH/KOH, followed by hydrolysis with 35% KOH; also from 6-chloro-3-methoxytoluene by oxidn. with $KMnO_4$ (5), or from 6-chloro-3-methoxybenzaldehyde by oxidn. with alk. $KMnO_4$ (8).]

3:4720 (1) Beyer, *Rec. trav. chim.* **40**, 628 (1921). (2) Mazzara, *Gazz. chim. ital.* **29**, I 376–379 (1899). (3) Minaev, Ripper, *Monatsh* **42**, 76–80 (1921); *J. Russ. Phys.-Chem. Soc.* **54**, 673–679 (1922/23); *Cent.* **1924**, I 905. (4) Minaev, *J. Russ. Phys.-Chem. Soc.* **58**, 113–118 (1926); *Cent.* **1926**, II 2295. (5) Peratoner, Condorelli, *Gazz. chim. ital.* **28**, I 214 (1898). (6) Coppadoro, *Gazz. chim. ital* **32**, I 547 (1902). (7) Plazek, *Roczniki Chem.* **10**, 761–776 (1930); *Cent.* **1931**, I 1428; *C.A.* **25**, 1504 (1931). (8) Hodgson, Beard, *J. Chem. Soc.* **1926**, 154. (9) Gibson, *J. Chem. Soc.* **1926**, 1428.

3:4725 1,1,1,2-TETRACHLORO-2-METHYLPROPANE



$C_4H_6Cl_4$ Beil. I-126 I_1— I_2—

M.P. 178.6–179.6° (1) **B.P. 192° cor. at 1175 mm. (1)**

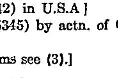
C̄ can be purified by sublimation or by recrystn. from alc.; difficult to separate, however, from 1,2,3-trichloro-2-methylpropane (3:5885), b p 162–163.1° (1). — C̄ is easily volatile with steam; eas. sol alc. or ether.

[For formn of C̄ (together with other products) from 1,1,2-trichloro-2-methylpropane (3:5710) or from *ter*-butyl chloride (3:7045) with Cl_2 see (1); for formn. of C̄ together with other products) from *β,β,β*-trichloro-*ter*-butyl alcohol ("Chloretone") (3:2662) + PCl_5 see (2).]

C̄ on htg. in s.t. with aq. at 180° yields (3) *α*-chloroisobutyric acid (3:0235).

3:4725 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1027–1029 (1936). (2) Willgerodt, Dürr, *Ber.* **20**, 539–540 (1887). (3) Willgerodt, Dürr, *J. prakt. Chem.* (2) **39**, 284 (1889).

3:4740 1,1,1,2,3-PENTACHLOROPROPANE
(*unsym.*-Pentachloropropane)



$C_3H_3Cl_5$ *Beil.* **I-107** I_1— I_2—

M.P. 179–180° (1)
178° (2)

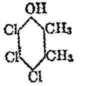
Colorless ndls. (from hot alc.) with camphoraceous odor. — Sublimes readily. — Insol. aq.; sol. org. solvents. [New comml. prod. (1942) in U.S.A.]

[For prepn. from 1,1,1-trichloropropene-2 (3:5345) by actn. of Cl_2 in diffuse light see (1).]

[For use as plasticizer with cellulose acetate films see (3).]

3:4740 (1) Victoria, *Rec. trav. chim.* **24**, 282 (1905). (2) Henry, *Rec. trav. chim.* **24**, 342 (1905). (3) Spicers, Ltd., Hand, Brit. 279,139, Nov. 17, 1927; French 125,165, Aug. 4, 1927; *Cent.* **1928**, I 770.

3:4742 4,5,6-TRICHLORO-2,3-DIMETHYLPHENOL (Trichloro-o-3-xylenol)



$C_8H_7OCl_3$

Beil. VI —
VI_1—
VI_2-(454)

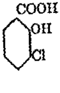
M.P. 180–181° (1)

Ndls. from dil alc. or lt pet.
[For prepn of C̄ from 5-chloro-2,3-dimethylphenol (5-chloro-o-3-xylenol) (3:2115) with Cl_2 in lt pet ether see (1).]

—— 4,5,6-Trichloro-2,3-dimethylphenyl acetate: unreported.
Ⓓ 4,5,6-Trichloro-2,3-dimethylphenyl benzoate: m.p. 128–129° (1).

3:4742 (1) Hinkel, Collins, Ayling, *J. Chem. Soc.* **123**, 2971 (1923).

3:4745 3-CHLORO-2-HYDROXYBENZOIC ACID (3-Chlorosalicylic acid)



$C_7H_5O_3Cl$

Beil. X - 101
X_1-(47)

M.P. 180–182°	(1)
180°	(2) (6)
178°	(3)
170°	(4)

Colorless ndls from aq. or dil alc ; 100 pts. aq. at 3 5° dis. 0 8 g. C̄; eas. sol. alc., AcOH, or $CHCl_3$. — Volatile with steam, sublimes with slight decompn.

[For prepn. of C̄ from o-chlorophenol (3:5980) by treatment of dry sodium salt with CO_2 at 140–150° under press. see (3), from 5-sulfo-2-hydroxybenzoic acid (5-sulfosalicylic acid) [Beil XI-411, XI_1-(106)] in AcOH with Cl_2 followed by hydrolysis of the resultant 3-chloro-2-hydroxy-5-sulfobenzoic acid with superheated steam (72% yield) see (1); from chloral-3-chlorosalicylamide (see below) by hydrolysis with 10 pts boilg 10% NaOH for 6 hrs. (86% yield) see (1), for formn. of C̄ from 7-chlorosaccharin (4) by NaOH fusion see (4); for formn from salicylic acid (1 .0780) in Na_2CO_3 soln. with Cl_2 (5-chloro-2-hydroxybenzoic acid (3 4705) is also formed) see (13)]

[For reactn. of C̄ with methylenedisalicylamide in prepn. of dye intermediates by oxidn. with $NaNO_2$ see (5)]

[C̄ on reductn with Na/Hg in pres. of H_3BO_3 yields(6) cf (7) 3-chloro-2-hydroxybenzaldehyde (3:1010); C̄ with $ClSO_3H$ at 50–70° yields (8) 5-chlorosulfonyl-3-chloro-2-hydroxybenzoic acid, cryst from $CHCl_3$, m p. 163–164° (8), which with Zn dust in alc. yields (9) 3,3′-dichloro-4,4′-dihydroxy-5,5′-dicarboxydiphenyl disulfide, m p. 258–259° (9), which in turn with alk. $Na_2S_2O_4$ undergoes reductive cleavage to 3-chloro-2-hydroxy-5-thiolbenzoic acid (3-chloro-5-thiolsalicylic acid), m p 210° (9)]

[C̄ with PCl_5 in low-boilg. pet ether yields (2) 3-chlorosalicyloyl chloride, ndls. from pet ether, m p 62–63° (2); this prod. on htg. yields (2) a mixt. of 3-chlorosalicylids: C̄ with PCl_3 yields (2) 6-chloro-2-chloroformylphenyl metaphosphite $Cl.CO.C_6H_3Cl.O.PO$, m p. abt. 65° (2)]

C̄ in aq soln gives with $FeCl_3$ an intense violet color.

Salts. NaĀ (3), KĀ (1), $CaĀ_2.3H_2O$ (1); $BaĀ_2.3H_2O$ (3), AgĀ (1); for details see indic refs.

—— Methyl 3-chloro-2-hydroxybenzoate (methyl 3-chlorosalicylate): ndls. from MeOH, m.p. 38° (2), b.p. 259–260° sl. dec. (3). [From $\bar{C}$ in MeOH with HCl gas (3), or from 3-chlorosalicyloyl chloride (above) in MeOH (2).] [For formn. from methyl salicylate (1:1750) with chloropicrin under influence of light see (10) (11).]

—— Ethyl 3-chloro-2-hydroxybenzoate (ethyl 3-chlorosalicylate): ndls. from cold alc., m.p. 21° (2), b.p. 269–270° (2), 147° at 12 mm. (2). [From 3-chlorosalicyloyl chloride (above) with EtOH (2).]

Ⓓ 3-Chloro-2-methoxybenzoic acid: white ndls. from alc., m.p. 120–121° (1). [From $\bar{C}$ in dil. aq. KOH by shaking with Me_2SO_4 in cold, followed by hydrol. of the intermed. ether-ester with hot aq. KOH and subsequent acidif. (1).] — [For nitration with mixt. of HNO_3 ($D = 1.5$) + conc. H_2SO_4 at 20–30° giving (100% yield) 3-chloro-2-methoxy-5-nitrobenzoic acid, m.p. 155.5°, see (14).]

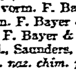
Ⓓ 3-Chloro-2-hydroxybenzamide (3-chlorosalicylamide): white ndls. from dil. alc., m.p. 174–175° (1). [From methyl 3-chlorosalicylate (above) or from 3-chlorosalicyloyl chloride (above) with conc. aq. NH_4OH in cold (1).] — [This prod. with chloral (3:5210) gives on warming (12) chloral-3-chlorosalicylamide, colorless ndls. from alc., m.p. 159–160° (12) (1), also obtd. from chloral-salicylamide in AcOH with Cl_2 (1).]

Ⓓ 3-Chloro-2-hydroxybenzanilide (3-chlorosalicylanilide): colorless ndls. from alc., m.p. 158.5–159° (2). [From 3-chlorosalicyloyl chloride (above) with 2 moles aniline in ether soln. (2).]

3:4745 (1) Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci.* A-8, 208–213 (1938). (2) Anschütz, Anspach, *Ann.* **346**, 312–317 (1906). (3) Varnholt, *J. prakt. Chem.* (2) **36**, 22–24 (1887). (4) Reissert, Cramer, *Ber.* **61**, 2565 (1928). (5) Durand, Huguenin, Brit. 183,123, Sept. 6, 1922; *Cent.* **1922**, IV 1171. (6) Farbenfabriken vorm. F. Bayer & Co., Ger. 228,838, Nov. 22, 1910; *Cent.* **1911**, I 51. (7) Farbenfabriken vorm. F. Bayer & Co., Ger. 216,305, Nov. 9, 1909; *Cent.* **1909**, II 2107. (8) Farbenfabriken vorm. F. Bayer & Co., Ger. 264,786, Sept. 23, 1913; *Cent.* **1913**, II 1350. (9) British Dyestuffs, Ltd., Saunders, Mendoza, Brit. 260,058, Nov. 18, 1926; *Cent.* **1929**, I 149. (10) Piutti, *Atti congr. naz. chim. pura applicata* **1923**, 398, 437–438; *Cent.* **1924**, I 2514.

(11) Piutti, Badolato, *Atti accad. Lincei* (5) **33**, I 475–479; *Cent.* **1924**, II 1893. (12) Hirwe, Rana, *Ber.* **72**, 1351 (1939). (13) Tischenko, *J. Russ. Phys.-Chem. Soc.* **60**, 153–162 (1928); *Cent.* **1928**, II 768; *C.A.* **22**, 3397 (1928). (14) Davies, Rubenstein, *J. Chem. Soc.* **123**, 2851–2852 (1923).

3:4747 2,5,6-TRICHLORO-3,4-DIMETHYLPHENOL (Trichloro-o-4-xylenol)



$C_8H_7OCl_3$ Beil. VI — VI_1— VI_2-(456)

M.P. 182.5° (1)

Ndls. from pet. ether.

[For prepn. of $\bar{C}$ from 5-chloro-3,4-dimethylphenol (6-chloro-o-4-xylenol) (3:2705) with Cl_2 in $CHCl_3$ see (1).]

—— 2,5,6-Trichloro-3,4-dimethylphenyl acetate: unreported.

Ⓓ 2,5,6-Trichloro-3,4-dimethylphenyl benzoate: m.p. 120° (1)

3:4747 (1) Hinkel, *J. Chem. Soc.* **125**, 1853 (1924).

 [illegible]
(1,2,[illegible]
tetra[illegible]
tetra[illegible]

acidification gives [illegible]
325], ndls. with 1 [illegible]
or AcOH soln [illegible]
chloroindone") [illegible]
of $\bar{C}$ with $Ca(O$[illegible]

M.P. 187° dec. [illegible]
182° [illegible]
180.5–181.5° [illegible]
170–180° [illegible]

[Beil. VIII-29[illegible]

[See also 5,6,7,8-tetrachloro-1,2,[illegible]

droxynaphth[illegible] [illegible], m.p. ab[illegible]

naphthalene[illegible]

adiene-1,3[illegible]

Cryst. from $CHCl_3$ or ether. — [illegible] For data on crystallographic [illegible] (6) (7). — For 2.39% soln. of $\bar{C}$ in [illegible]

[For prepn of $\bar{C}$ from naphthalene [illegible] refluxed 3 hrs. (15% yield) see (1); [illegible] with $KClO_3$ + HCl see (13) (9); [illegible] numerous by-products are formed [illegible]

$\bar{C}$ on vigorous boilg in small quantities [illegible] lene (3:1655), m.p 68°; with larger [illegible]

$\bar{C}$ (3 pts.) with aq. (100 pts.) boiled for [illegible] after concn. deposits (65% yield (15)) a [illegible] [Beil. VI-971], cryst. from alc., m.p. [illegible] 148–150°) (15).

6). (3) [illegible]
1). (5) [illegible]
03–304 [illegible]
Brass, [illegible]

$\bar{C}$ with alc. KOH on boilg yields (2) (16) (17) [illegible] lene (3:1310), m p. 61–62°, accompanied by [illegible] 68°, and a little 2,3-dichloronaphthalene (3:[illegible] 38°, supposed by the earlier workers to have been [illegible] (19) to consist of a mixt. (possible mol cpd.) of [illegible] naphthalene.

$\bar{C}$ on oxidn. with 8.7 wt. pts. conc HNO_3 (D = 1.4[illegible]) at [illegible] (20) 2,3-dichloronaphthoquinone-1,4 (3:4857), m p. [illegible] HNO_3 also yields (21) (13) (presumably by further oxidn. of [illegible] acid (1·0820) and oxalic acid (1:0115).

$\bar{C}$ on oxidn. with CrO_3/AcOH yields (20) 2,4-dichloronaphth[illegible] 107° (20).

[$\bar{C}$ with moist silver oxide in s t. at 200° yields (19) (9) a [illegible] 2,3-dichloronaphthalene (3·3665), and other prods. (9).]

[$\bar{C}$ on nitration with HNO_3 (D = 1.5) at not above 20 [illegible], followed by [illegible] with $MeOH/Na_2CO_3$ or $MeOH/NaHCO_3$ in C_6H_6 at [illegible] with $MeOH/NH_3$ ord. temp (23), yields 5,8-dichloro-1-nitronaphthalene [Beil. [illegible] 2).]

[For conversion of $\bar{C}$ to artificial resins by htg. with metal halides such as [illegible]), or by htg with naphthalene + a surface cat. such as fuller's earth (25), see [illegible]

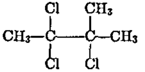
[4]750 (1) Pongratz, Eichler, Ber. 69, 1295 (1936). (2) Faust, [illegible], Ann. [illegible] Klingstedt, Wiese, Hudlick, Acta Acad. Aboensis Math. et Phys. [illegible], I 501; C.A. 23, 1399 (1929). (4) Hintze, J. prakt. Chem. (2) [illegible] (6)

Groth, *Chem. Krystalog.* **5**, 368 (1919). (6) Robertson, *Proc. Roy. Soc.* (*London*) **118-A**, 709–727 (1928). (7) Bragg, *Z. Krist.* **66**, 27–32 (1927). (8) Kanonnikoff, *J. prakt. Chem.* (2) **31**, 342–343 (1885). (9) Leeds, Everhart, *J. Am. Chem. Soc.* **2**, 207–209, 210–213 (1880). (10) Laurent, *Ann. chim.* (2) **52**, 275–281 (1833); **59**, 201–204 (1835).

(11) Paul, Depoully, *Bull. soc. chim.* (2) **4**, 10–12 (1865). (12) Schwarzer, *Ber.* **10**, 379 (1877). (13) Fischer, *Ber.* **11**, 735–741, 1411–1412 (1878). (14) Krafft, Becker, *Ber.* **9**, 1088–1090 (1876). (15) Grimaux, *Bull. soc. chim.* (2) **18**, 205–212 (1872); *Compt. rend.* **75**, 352–355 (1872). (16) Widman, *Ber.* **15**, 2161–2162 (1882). (17) Cleve, *Ber.* **23**, 954 (1890). (18) Armstrong, Wynne, *Chem. News* **58**, 264–265 (1888). (19) Armstrong, Wynne, *Chem. News* **61**, 273, 284 (1890); *Proc. Chem. Soc.* (*London*) **4**, 106 (1888). (20) Helbig, *Ber.* **28**, 505–507 (1895).

(21) Laurent, *Ann chim.* (2) **74**, 26–27 (1840); *Ann.* **35**, 292–293 (1840). (22) Matter, Ger. 317,755, Dec. 29, 1919; *Cent.* **1920**, II 601. (23) Matter, Ger. 348,069, Jan. 28, 1922; *Cent.* **1922**, IV 45. (24) A G.F.A., Ger. 332,391, Feb. 2, 1921; *Cent.* **1921**, II 652; Ger. 334,710, March 17, 1921; *Cent.* **1921**, II 964. (25) Schering-Kahlbaum, Freund, Jordan, Ger. 461,358, June 20, 1928; *Cent.* **1929**, I 1052, Brit. 202,997, Oct. 24, 1924, *Cent.* **1925**, I 1456.

3:4755 2,3,3-TRICHLORO-2-METHYLBUTANE



$C_5H_9Cl_3$ **Beil. I-135**
I_1—
I_2—

M.P. 182–183° (1)
abt. 170° (2)

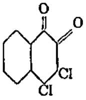
[For prepn. of C̄ from 2-chloro-2-methylbutane (3:7220) or from 2,3-dichloro-2-methylbutane (3:7975) with Cl_2 see (2); for formn. from 3-chloro-2-methylbutene-2 (3:7335) + Cl_2 (10% yield together with other prods.) see (1) (an earlier product (3) obtd by this latter method and to which this structure was assigned was reported as a liquid, b.p. 176°, D_4^{15} = 1.215, n_D^{21} = 1.472).]

C̄ is not (2) saponified by 20% aq. K_2CO_3.

C̄ on htg. with 2 moles quinoline at 195–225° gives (60% yield (2)) β-chloroisoprene (3:7290).

3:4755 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223, *C.A.* **33**, 4190 (1939). (2) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936); *Cent.* **1937**, I 573; *C.A.* **31**, 1003 (1937). (3) Brochet, *Ann. chim.* (7) **10**, 385 (1897).

3:4775 3,4-DICHLORONAPHTHOQUINONE-1,2



$C_{10}H_4O_2Cl_2$ **Beil. VII-721**
VII_1—

M.P. 184–185° (1)
184° (1) (2) (3)
183° (6)

Red tbls. or ndls from AcOH, C_6H_6 or $CHCl_3$. — Spar. sol. alc., fairly eas. sol. $CHCl_3$ — Sublimes undecomposed.

[For prepn. of C̄ from 1-aminonaphthol-2 hydrochloride [Beil. XIII-676, $XIII_1$-(274)], in AcOH with Cl_2 (68.5% yield (3)) (2) (4), or from naphthoquinone-1,2 (1:9062) in AcOH with Cl_2 (2), see indiv. refs ; for formn. of C̄ from 3,4-dichloro-naphthoquinone-1,2-oxime-1 (3,4-dichloro-1-nitroso-naphthol-2) [Beil. VII-721] on oxidn. with conc. HNO_3 in AcOH soln. see (5); from 3,4-dichloro-3-nitro-1,2-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-701] with AcCl in s.t. at 100° see (6).]

C̄ dis. in cold dil. aq. alk. yielding colorless soln. which upon acidification gives (90% yield (4)) ... acid-3 [Beil. X-325], ndls with 1 H_2O (from dil. ... on oxidn. in dil. aq. or AcOH soln. with CrO_3 gives ... ndene-1-one-3 ("dichloroindone") [Beil. VII-384], gold-yel. ndls from alc. or AcOH, m.p. 89–90°.] [For behavior of C̄ with $Ca(OCl_2)$ soln. see (7).]

C̄ with alc. NaOEt yields (8) 3-chloro-4-ethoxynaphthoquinone-1,2, [Beil. VIII-299], or.-red ndls. from alc., m.p. 149° (8).

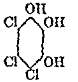
C̄ in hot alc. soln. on treatment with alc. NH_3 yields (2) 3-chloro-2-hydroxynaphthoquinone-1,4-imide-4 (4-amino-3-chloronaphthoquinone-1,2) [Beil. VIII-305], m.p. abt. 260° (2).

C̄ in dil. AcOH with excess SO_2 (2) reduces to 3,4-dichloro-1,2-dihydroxynaphthalene [Beil. VI-975], m.p. 125° (2).

[For cpd. formn. of C̄ with $SnCl_4$ see (9); for reactn. of C̄ with 2,3-dimethylbutadiene-1,3 in $CHCl_3$ see (10).]

3:4775 (1) Zincke, *Ann.* **257**, 146–147 (1890). (2) Zincke, *Ber.* **19**, 2499–2500 (1886). (3) Brass, Mosl, *Ber.* **59**, 1271 (1926). (4) Zincke, Engelhardt, *Ann.* **283**, 347–349 (1894). (5) Zincke, Schmunk, *Ann.* **257**, 146–147 (1890). (6) Zincke, Scharfenberg, *Ann.* **268**, 303–304 (1892). (7) Zincke, Schmidt, *Ber.* **27**, 744 (1894). (8) Hirsch, *Ber.* **33**, 2114 (1900). (9) Brass, Fengler, *Ber.* **64**, 1663–1664 (1931). (10) Fieser, Dunn, *J. Am. Chem. Soc.* **59**, 1020 (1937).

3:4782 4,5,6-TRICHLOROPYROGALLOL



$C_6H_3O_3Cl_3$ **Beil. VI-1084**
VI₁—
VI₂—

M.P. about	**185°** dec.	(1)
	177° u.c. dec.	(2)
	175°	(3)

Ndls. with 3 H_2O, m.p. 75° (1) from alc. or C_6H_6 (2); this trihydrate in vac. over H_2SO_4 loses 2 H_2O, the final H_2O at 110° (2). — C̄ is spar. sol. in cold aq., C_6H_6, $CHCl_3$, CCl_4, or CS_2; eas. sol. alc., ether, or hot aq.

[For prepn. of C̄ from pyrogallol (1,2,3-trihydroxybenzene) (1:1555) in 60% AcOH with Cl_2 (2), or with SO_2Cl_2 in dry ether (3), see indic. refs.]

[For prepn. of C̄ from "leucogallol" [Beil. VI-1078] or "mairogallol" [Beil. VI-1078] by reduction with Zn dust + dil. H_2SO_4 see (1); from gallic acid (1:0875) in $CHCl_3$ with Cl_2 see (4).]

[C̄ in CCl_4 or $CHCl_3$ prev. satd. with Cl_2 gives (2) "leucogallol."]

C̄ in ether soln. with aq. $Ba(OH)_2$ gives deep blue coloration; with aq. Na_2SO_3 a fugitive red coloration (2).

C̄ with aq. $FeCl_3$ gives (4) a blue coloration.

C̄ with conc. HNO_3 is oxidized and decomposed (2); C̄ dis. in cold conc. H_2SO_4 without evoln. of gas but on warming decomposes (2).

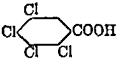
C̄ reduces $NH_4OH/AgNO_3$ (1).

—— 4,5,6-Trichloropyrogallol trimethyl ether: cryst. from alc., m.p. 54° (5). [Prepd. indirectly (5).]

... 125° (4), 122° (1).

3:4782 (1) Hantzsch, Schniter, *Ber.* **20**, 2034–2037 (1887). (2) Webster, *J. Chem. Soc.* **45**, 205–208 (1884). (3) Peratoner, Condorelli, *Gazz. chim. ital.* **28**, I 225–226 (1898). (4) Bietrix, *Bull. soc. chim.* (3) **15**, 904–906 (1896). (5) Bartolotti, *Gazz. chim. ital.* **27**, I 290–291 (1897).

3:4790 2,3,4,5-TETRACHLORO-BENZOIC ACID



$C_7H_2O_2Cl_4$ Beil. IX-346; IX_1—

M.P. 186° (1)

Ndls. from alc. — Eas. sol. alc., ether; spar. sol. aq.

[For prepn. of C̄ from tetrachlorophthalic acid (3:4946) by htg. with 2–3 pts. AcOH in s.t. at 300° for 3–4 hrs. see (1); by htg. with steam + H_2 at 200–400° over decarboxylating cat. see (2).]

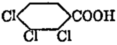
C̄ on ½ hr. boilg. with mixt. of 2 pts. HNO_3 (D = 1.48) + 1 pt. conc. H_2SO_4 gives (100% yield (1)) 2,3,4,5-tetrachloro-2-nitrobenzoic acid [Beil. IX-405], lfts. from aq., but no m.p. has been reported.

Neither the action (if any) of PCl_5 or $SOCl_2$ on C̄ nor the expected 2,3,4,5-tetrachlorobenzoyl chloride has been recorded.

—— **Methyl 2,3,4,5-tetrachlorobenzoate:** unrecorded.
—— **Ethyl 2,3,4,5-tetrachlorobenzoate:** from C̄ + EtOH + HCl gas; ndls. alc., m.p. 34.5° (1).
—— **2,3,4,5-Tetrachlorobenzamide:** unrecorded.
—— **2,3,4,5-Tetrachlorobenzanilide:** unrecorded.

3:4790 (1) Tust, *Ber.* **20**, 2430–2431 (1887). (2) Jaeger (to Selden Co.), U.S. 1,953,232, April 3, 1934; *Cent.* **1934**, II 669; *C.A.* **28**, 3743 (1934).

3:4810 2,3,4-TRICHLOROBENZOIC ACID



$C_7H_3O_2Cl_3$ Beil. IX-345; IX_1—

M.P. 186–187° (1)

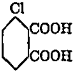
Ndls. from hot aq. (1). — C̄ does *not* melt under boiling water (1).

[For prepn. from 2,3,4-trichlorotoluene (3:0425) by oxidn. with HNO_3 in s.t. at 150° see (1); from 2,3,4-trichlorobenzaldehyde (3:2445) by oxidn. with $KMnO_4$ see (2).] [The latter product was probably impure (1).]

No further data on C̄ are recorded.

3:4810 (1) Cohen, Dakin, *J. Chem. Soc.* **81**, 1328 (1902). (2) Seelig, *Ann.* **237**, 150 (1887).

3:4820 3-CHLOROPHTHALIC ACID



$C_8H_5O_4Cl$ Beil. IX-816; IX_1-(360)

M.P. **186–187°** (1)
185–187° (2)
186° (3)
184° (4) (5)

[*See also 3-chlorophthalic anhydride* (3:3900).]

Ndls from aq.; eas. sol. alc.; eas. sol. ether (use in sepn. from phthalic acid (1:0820) (6). — 100 pts. aq. at 14° dis. 2.16 pts. C̄ (5). — [For sepn. of C̄ from o-chlorobenzoic acid (3:4150) by use of $CHCl_3$ see (7).]

[For prepn. of C̄ from 3-chlorophthalic anhydride (3:3900) by hydrolysis with boilg. dil. HCl see (3) (6); from 1,5-dichloronaphthalene (3:3200) by oxidn. with CrO_3/AcOH see (5); from 5-chloro-1,2,3,4-tetrahydronaphthalene [Beil. V_1-(237)] (1) by oxidn. with $KMnO_4$ see (1); from 3-chloro-2-methylbenzoic acid (3:4435) by oxidn. with $KMnO_4$ see (8).]

C̄ on htg above its m p yields (5) (8) 3-chlorophthalic anhydride (3:3900).

[C̄ on KOH fusion yields (8) (note rearrangement.) 4-hydroxyphthalic acid [Beil. X-499, X_1-(255)], m p. 204–205°, with conv. to corresp. anhydride, m.p 171°.]

[C̄ with steam passed over cat. at 350° loses CO_2 presumably yielding (9) o-chlorobenzoic acid (3:4150) and/or m-chlorobenzoic acid (3:4392).]

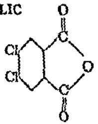
[C̄ htd. with $Hg(OAc)_2$ in AcOH as directed (2) gives *anhydro*-2-hydroxymercuri-3-chlorobenzoic acid which on htg with aq HCl yields m-chlorobenzoic acid (3·4392)]

Salts. $Ag_2\bar{A}$, ndls. from hot aq. (5); $Ba\bar{A}$, eas sol. cold aq, but spar. sol. hot aq., on protracted boilg. with aq gives monohydrate which is insol cold aq. (8).

Esters. The neutral dimethyl and diethyl esters of C̄ are unreported; of the various possible acid esters only ethyl hydrogen 3-chlorophthalate, m p. 118–119° (1), has been reported.

3:4820 (1) von Braun, Larbig, Kredel, *Ber.* **56**, 2337–2338 (1923). (2) Whitmore, Culhane, *J. Am. Chem Soc.* **51**, 602–605 (1929). (3) Bogert, Boroschek, *J. Am Chem Soc* **23**, 751 (1901). (4) Egerer, Meyer, *Monatsh.* **34**, 81 (1913). (5) Guareschi, *Gazz. chim. ital.* **17**, 120–122 (1887). (6) Smith, *J Chem. Soc.* **1933**, 1643–1644. (7) Jaeger (to Selden Co), U.S. 1,685,634, Sept. 25, 1928; *Cent.* **1929**, I 807. (8) Krüger, *Ber.* **18**, 1759 (1885). (9) Jaeger (to Selden Co.), U.S. 1,953,231, April 3, 1934, *Cent.* **1934**, II 1688.

3:4830 4,5-DICHLOROPHTHALIC ANHYDRIDE $C_8H_2O_3Cl_2$ Beil. XVII - 483 $XVII_1$-(254)



M.P. 187.5–188° cor.	(1)	B.P. 313° (4)
187°	(2) (3)	
185–187°	(4)	
185°	(6)	

[*See also 4,5-dichlorophthalic acid* (3:4890).]

Tbls. or pr. from hot toluene or from CCl_4; spar. sol. cold but eas. sol. hot C_6H_6 or toluene; very little sol in CCl_4

[For prepn. of C̄ from 4,5-dichlorophthalic acid (3:4890) by htg at 200° (4) or by htg. with AcCl (2) see indic. refs.; for formn. of C̄ (together with other isomers) from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe or Fe salts at 160–260° (5), or from phthalic anhydride (1:0725) or 3-chlorophthalic anhydride (3:3900) with Cl_2 in fumg. H_2SO_4 in pres. of I_2 (4) (1), see indic. refs.; for formn. of C̄ from aq solns. of alk. salts of phthalic acid (1:0820) with Cl_2 see (2) (6) (7).]

[For sepn. of C̄ from isomeric dichlorophthalic anhydrides by means of salts of corresp.

acids, etc., see (4) (8) (1); by means of differential hydrolysis with H_2SO_4 (prods. with no α chlorine such as C̄ require H_2SO_4 of 98–100% concn., those with 1 α chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56–95% H_2SO_4, those with 2 α chlorine atoms such as 3,6-dichloro- or 3,4,5,6-tetrachlorophthalic anhydrides hydrolyze at H_2SO_4 concns. of less than 50%) see (9).]

C̄ dislvd. in abs. alc. yields (4) ethyl hydrogen 4,5-dichlorophthalate, ndls. from $CHCl_3$, m.p. 133–134° (4).

[C̄ with 1 mole $NH_2OH.HCl$ + Na_2CO_3 in aq. soln. as directed (4) yields 4,5-dichlorophthaloylhydroxylamine (*N*-hydroxy-4,5-dichlorophthalimide) [Beil. XXI-504], pr. from MeOH, m.p. 195–197° dec. (4); this prod. on warming with aq. Na_2CO_3 gives 100% yield 4,5-dichloro-2-aminobenzoic acid (4,5-dichloroanthranilic acid) [Beil. XIV-368, XIV_1-(549)], m.p. 213–214° (4).]

[C̄ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (10) 3,4-dichlorobenzoic acid (3:4925).]

C̄ with benzene + $AlCl_3$ (12) or in acetylene tetrachloride (11) gives (98% yield (12)) 4,5-dichloro-2-(*o*-benzoyl)benzoic acid [Beil. X_1-(357)], cryst. from C_6H_6 (12) or toluene (11), m.p. 209° (12), 208° (11), which on htg with 20 pts. conc. H_2SO_4 at 160° for 1 hr. gives (92% yield (12)) (11) 2,3-dichloroanthraquinone [Beil. VII-788, VII_1-(413)], yellowish ndls. from AcOH, m.p. 267° cor. (12), 265° (11). — [C̄ with *o*-xylene + $AlCl_3$ in acetylene tetrachloride gives (80% yield (11)) 4,5-dichloro-2-(3′,4′-dimethylbenzoyl)benzoic acid, cryst. from cyclohexane, m.p. 184° (11), which with 10 pts. conc. H_2SO_4 at 100° gives (45% yield (11)) 6,7-dichloro-2,3-dimethylanthraquinone, cryst. from xylene, m.p. 305° (11). — C̄ with *o*-dichlorobenzene (3:6055) + $AlCl_3$ 4 hrs. at 100° gives (80% yield (11)) 3,4-dichloro-2-(3′,4′-dichlorobenzoyl)benzoic acid, cryst. from C_6H_6, m.p. 183°, which with 12 pts. conc. H_2SO_4 6 hrs. at 100° gives mainly 2,3,6,7-tetrachloroanthraquinone, cryst. from *o*-dichlorobenzene, m.p. 348° (11). — For analogous reactns. of C̄ with naphthalene (13), pyrene (14), or *o*-chlorotoluene (15) see indic. refs.]

[C̄ with hydroquinone (1:1590) + H_3BO_3 htd. at 190° and afterward treated with hot conc. H_2SO_4 at 150–165° (16), or C̄ with $AlCl_3$ + NaCl htd. at 200–220° (17), or C̄ with *p*-chlorophenol (3:0475) htd. with fumg. H_2SO_4 + H_3BO_3 (18) gives (yield: 80% (17), 15% (16)) 6,7-dichloro-1,4-dihydroxyanthraquinone (6,7-dichloroquinizarin) [Beil. VIII-452, $VIII_1$-(716)], red-br. cryst. from xylene, m.p. 295.5° (17), 288° (16), (diacetate, m.p. 125° (16), dimethyl ether, m.p. 168 5° (17)).]

[For use of C̄ in prepn. of pigments of the copper phthalocyanine type see (19).]

C̄ with $(NH_4)_2CO_3$ htd at 250° for ½ hr. (20) yields 4,5-dichlorophthalimide, pl. from alc., m.p. 221° (20) (note that behavior of C̄ with conc aq. NH_4OH is different yielding (4) 4,5-dichlorophthalamic acid (not specifically characterized) which with alk. NaOCl gives 4,5-dichloro-2-aminobenzoic acid (above)). — [For behavior of C̄ with hydrazine hydrate in AcOH yielding corresp. cyclohydrazide see (21).]

C̄ (1 pt.) in boilg. AcOH (6 pts.) treated with aniline (1 pt.) gives (82% yield (1)) 4,5-dichlorophthalanil (*N*-phenyl-4,5-dichlorophthalimide) [Beil. XXI_1-(301)], cryst. from AcOH, m.p. 212.5–213° cor. (1).

C̄ on saponification with standard alkali (Sap. Eq. = 108 5), followed by acidification, yields 4,5-dichlorophthalic acid (3:4890) q.v

3:4830 (1) Pratt, Perkins, *J. Am. Chem. Soc.* **40**, 215–216, 218 (1918). (2) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 1876. (3) Ayling, *J. Chem. Soc.* **1929**, 255. (4) Villiger, *Ber.* **42**, 3538–3539, 3546–3549 (1909). (5) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* **1936**, I 2830; *C.A.* **30**, 1391 (1936). (6) Rushchinskii, *J. Applied Chem.* (*U.S.S.R.*) **7**, 1113–1115 (1934); *Cent.* **1936**, II 2902. (7) Rushchinskii, Russ 41,515, Feb. 28, 1935; *Cent.* **1935**, II 3704; *C.A.* **30**, 8247 (1936). (8) Hodgson, *J. Soc. Dyers Colourists* **49**, 215 (1933).

(9) Imperial Chem Ind, Ltd., French 749,954, Aug. 2, 1933; *Cent.* **1933**, II 2748–2749. (10) Jaeger (to Selden Co), U.S. 1,964,516, June 26, 1934; *Cent* **1934**, II 3047. (11) Barnett, Goodway, Watson, *Ber* **66**, 1878–1879, 1884–1889 (1933). (12) Ullmann, Billig, *Ann* **381**, 27–28 (1911). (13) Waldmann, *J. prakt Chem* (2) **131**, 79 (1931). (14) Verein für Chem. und Metallurg. Produktion, Czechoslovak. 46,835, Feb. 25, 1934; *Cent.* **1934**, II 518. (15) Keimatsu, Hirano, *J Pharm. Soc. Japan* **49**, 20–26 (1929); *Cent* **1929**, I 2533 (16) Frey, *Ber* **45**, 1363–1364 (1912). (17) Waldmann, *J prakt. Chem* (2) **126**, 253–254 (1930). (18) Scottish Dyes, Ltd, Bangham, Hooley, Thomas, Brit. 339,589, Jan. 8, 1931; *Cent.* **1932**, I 2095 (19) Imperial Chem. Ind., Ltd., French 808,845, Feb 16, 1937; Brit. 464,126, April 12, 1937, *Cent.* **1937**, II 3820, *C A.* **31**, 6255 (1937). (20) Drew, Pearman, *J. Chem. Soc* **1937**, 590

(21) Drew, Pearman, *J Chem. Soc.* **1937**, 32

3:4835 HEXACHLOROETHANE $Cl_3C\text{-}CCl_3$ C_2Cl_6 Beil. I - 87
(Perchloroethane) I_1-(26) I_2-(58)

M.P.		B.P.	
189° s.t.	(1)	**185.5°** at 776.7 mm.	(7)
187–188°	(74) (115)	**185°** at 760 mm.	(18)
187.71–188.75° cor., s.t.	(7)		
187° s.t.	(2) (3)		
187°	(4) (5) (6) (63) (64)		
186.85–187.4° cor., s.t.	(7)		
186.8°	(8)		
186–187°	(9) (133)		
186°	(10) (75)		
185–186°	(11)		
185°	(12) (13) (14) (132)		
183–184° s.t.	(15)		
183.0–184.0°	(16)		
181° s.t.	(17)		

White cryst. with camphoraceous odor which readily sublime without melting. — Cryst. from alc, ether, $CHCl_3$ or CS_2. — Č is trimorphous: below about 46° cryst. Č is orthorhombic, in range 46–71° cryst Č is triclinic; about 71° cryst Č is cubic at these transition temps volume alterations occur which have sometimes (5) been mistaken for m p.'s. — [For details on trimorphism and these transitions see (19) (8) (20) (21) (25) (26); for influence of high press. see (22) — For crystallographic data see (20) (23) (24); for X-ray crystallog. data see (27) (28)]

Č is almost abs. insol aq and vice versa at ord temp. (29); for patents on drying of Č see (30) (31) — [For studies of vap press of Č at various temps see (13) (4) (7) (32). — For prevention of "caking" of cryst Č by addn of 1–10% paraformaldehyde see (33)]

Cryoscopic const of Č, i.e, f p. lowering per mole solute in 100 g Č, is 5 6° (34). [For thermal anal. of binary systems of Č with naphthalene (1:7200) (8) (34), with phenanthrene (1:7240) (34), or with anthracene (1:7285) (34) see indic. refs]

USES OF Č

Č finds many uses in industry, some based on its physical characteristics and some on its chem. behavior — [E g, for use of Č as solvent for prepn. of solid solns. of I_2 for use in place of usual tincture see (35); for use of Č as means for temporary marking of cloth removable at will by heat (sublimation) see (36)]

[For use of $\bar{C}$ as addition agent to CCl_4 fire extinguishers see (37); as component of certain types of explosives (e.g., 75% nitrostarch + 20% $\bar{C}$ + 5% $NaNO_3$) see (38); for use of $\bar{C}$ as mothproofing agent see (39) (40) (41) (42); for use of $\bar{C}$ as insecticide and/or fungicide see (43) (44); for use of $\bar{C}$ together with CS_2 (45) or rotenone (46) as insecticides see indic. refs.]

$\bar{C}$ is an important component of "HC" smoke candles or grenades used for the production of screening clouds or smokes; a mixture of $\bar{C}$ with powdered metal (usually Zn) once started undergoes vigorous decomposition yielding $ZnCl_2$ + C; other materials are usually added to ignite the mixture and to modify the character of the resultant smoke; for further details see (47) (48) (49). — [For use of this type of reactn. in prepn. of activated carbon see (153)]

PHYSIOLOGICAL ASPECTS OF $\bar{C}$

[For studies of toxicity of $\bar{C}$ and its ability to penetrate skin see (50) (51) (52) cf. (160); for studies of $\bar{C}$ as anthelmintic see (53) (54); for study of antiseptic power of $\bar{C}$ see (55).]

DETERMINATION OF $\bar{C}$

For detn. of $\bar{C}$ by reactn. with Na + ethanolamine in dioxane followed by detn. of resultant chloride ion see (161).

PREPARATION (OR FORMATION) OF $\bar{C}$

$\bar{C}$ is a by-product of the tech. prepn. of CCl_4 (5:5100) from CS_2 + Cl_2 (56), of prepn. of $CHCl_3$ (3:5050) and of CH_2Cl_2 (3:5020) (57), and is found (12) (together with other by-products) in the high-boilg. fractn. ("Tri-Nachlauf") from the prepn. of trichloroethylene (3:5170) from acetylene tetrachloride (3:5750). — For quick prepn. of $\bar{C}$ from CCl_4 (3:5100) refluxed with Al powder (80% yield (14)) or with Al/Hg (65% yield (58)) cf. (96) see indic. refs.; for prepn. of $\bar{C}$ from ethylene with Cl_2 over activated carbon at 300–350° (90% yield) see (59). — For many other methods of preparation, manufacture, or formation see below.

From various polychloroethanes. *From 1,2-dichloroethane (ethylene dichloride) (3:5130).* [For prepn. of $\bar{C}$ from ethylene dichloride in vapor phase with Cl_2 + cat. (60) (61) or with Cl_2 under press. (62) see indic. refs.; note that ethylene dichloride in liq phase with Cl_2 gives mainly (61) 1,1,2-trichloroethane (3:5085). — Note also that 1,2-dibromoethane (ethylene dibromide) refluxed with $AlCl_3$ while treated with Cl_2 (63) gives $\bar{C}$.]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [For formn. of $\bar{C}$ together with other prods. from acetylene tetrachloride over pumice at 700° (64), or with anhydr. $FeCl_3$ on htg. in s.t. (65), or with Cl_2 (66) in u.v. light at 50–60° (67) or X-radiation (68), or with Cl_2 over activated carbon at 300–400° (69) (70) or at 60–70° (71), or with Cl_2 in pres. of $AlCl_3$ at 20–100° (71) or at 120° under reflux (80% yield (72)), or with Cl_2 in pres. of Fe at 20–80° (71), or with Cl_2 in CCl_4 soln. (73), or even with aq. bleaching powder (71), see indic. refs. — (Note also that acetylene tetra*bromide* with $AlCl_3$ + Cl_2 under reflux yields (63) $\bar{C}$).]

From pentachloroethane (3:5880). [For formn. of $\bar{C}$ together with other prods. from pentachloroethane with dry Cl_2 + AlCl... or with ... carbon at 300–400° (70), or with Cl_2 in u.v. ... exce... 10 hrs. (16), see indic. refs. — (Note also that ... SbC... for 2 hrs. gives (75) $\bar{C}$.)]

From various ... *...ene (3:5170).* [For formn. of $\bar{C}$ ... over

pumice at 700° (64), or with anhydrous $FeCl_3$ on htg. in s.t. (65), or with Cl_2 over act. carbon at 60–70° (98% yield (70)), see indic. refs.]

From tetrachloroethylene (3:5460). [For prepn. and/or formn. of $\bar{C}$ from tetrachloroethylene with Cl_2 (162) (76) (77) in direct sunlight (78) cf. (79) (80) (106) or in pres. of suitable cat. in dark at 80–100° (81), or in CCl_4 soln. at 22° (82) cf. (73) or in vapor phase at 40° and low press. in light and absence of oxygen (33) see indic. refs. (note that tetrachloroethylene (3:5460) with Cl_2 + light in presence of O_2 undergoes photo-oxidation to trichloroacetyl chloride (3:5420)). — For formn. of $\bar{C}$ from tetrachloroethylene with SO_2Cl_2 in pres. of dibenzoyl peroxide (84), or in small amt. with dibenzoyl peroxide alone (85), or with chlorine monoxide in CCl_4 at −20° (86), see indic. refs.] See also below under formn. of $\bar{C}$ from acetylene.

From dichloroacetylene (3:5010). [For formn. of $\bar{C}$ from dichloroacetylene with Cl_2 in CCl_4 soln. see (2).]

From various polychloromethanes. *From trichloromethane (chloroform) (3:5050).* [For formn. of $\bar{C}$ together with other prods. from $CHCl_3$ by pyrolysis at 425° (87), in electric arc (6), by actn. of radium radiation (88), or by actn. of NCl_3 in sunlight (89) see indic. refs.]

From carbon tetrachloride (3:5100). [For formn. of $\bar{C}$ together with other prods. from CCl_4 by pyrolysis at 600–1500° (90) cf. (91) (76), by actn. of electric arc (6), dark elec. discharge (92), or radium radiation (88), with hydrogen at 600–650° (93), or with hydrogen over reduced Ni at 270° (94), or from CCl_4 in nitrogen over GeO_2 at 500–865° (95), see indic. refs.]

[For prepn. of $\bar{C}$ from CCl_4 (3:5100) by refluxing with Al powder (80% yield (14)), Al/Hg (65% yield (58)), or Al + $AlCl_3$ (96), or by htg. with Cu powder in s.t. at 120° (97), amorphous As in s.t. at 160° (98), or molecular Ag in s.t. at 200° (99), see indic. refs.]

From various hydrocarbons. *From methane.* [For formn. of $\bar{C}$ together with other prods. from CH_4 + Cl_2 in silent elec. discharge see (100).]

From ethane. [For formn. of $\bar{C}$ together with other prods. from ethane with Cl_2 in pres. of activated carbon or other cat. at elev. temp. see (101) (102) (103).]

From ethylene. [For formn. of $\bar{C}$ together with other prods. from ethylene with Cl_2 over act. carbon at 120–125° (104) or at 300–350° (90% yield (59)) cf. (101) (105).]

From acetylene. [For formn. of $\bar{C}$ together with other prods. from acetylene with Cl_2 at 650–1000° as directed (106) or at 700–950° as directed (107), with Cl_2 in an inert gas such as N_2 or HCl over act. carbon at elev. temp. (108), or with S_2Cl_2 in pres. of 1–2% reduced iron (109) (110) see indic. refs. — (Note that by this mode of procedure acetylene tetrachloride (see this heading above) is a probable intermediate.)]

From miscellaneous sources. $\bar{C}$ has been observed as one of the products of decomposition of many different types of compounds contg. the $-CCl_3$ group [For example, for formn. of $\bar{C}$ (together with other prods.) from iodotrichloromethane on distn. (111), from bromotrichloromethane in ultraviolet light (112), from trichloroacetyl chloride (3:5420) at 600° (113), from trichloroacetyl bromide in s.t. at 400° (113), from trichloroacetyl iodide on distn. at ord. press. (113), from nitrosotrichloromethane with O_2 at 120° (114), or from nitrotrichloromethane (chloropicrin) with HCl gas over pumice at 400° (1) see indic. refs. — For formn. of $\bar{C}$ together with other prods. from trichloroacetaldehyde (chloral) (3:5210) with Cl_2, Br_2, or I_2 in pres. of $AlCl_3$ (115), from trichloroacetic acid (3:1150) by pyrolysis over ThO_2, kaolin, or carbon (116), from K trichloroacetate by electrolysis of its soln. in aq. KOAc (15), from ferric trichloroacetate in aq. soln. in light (117) (118) (119), from pentachlorodimethyl ether on htg. with aq. (120), or from trichloromethyl benzoate on htg. (121) see indic. refs.]

The formn. of $\bar{C}$ has also been observed in connection with certain acid chlorides [e.g.,

for formn. of $\bar{C}$ from acetyl chloride (3:7065) with excess PCl_5 in s.t. at 180° (122), from pentachloropropionyl chloride (3:0470) with $AlCl_3$ on warming (123), from dichloromaleyl (di)chloride (3:6197) with PCl_5 at 230° for 6 hrs. (124), or from pentachloroethyl chloroformate with $AlCl_3$ at 100° (125) see indic. refs.]

[For formn. of $\bar{C}$ from various alkanes with $SbCl_5 + I_2$ (126), from a mixt. of dichloropropanes or from hexachlorobutadiene (3:6425) with Cl_2 at 400° and 30 atm. (127), from an electric arc between carbon electrodes in Cl_2 (128), from n-propyl chloride (3:7040) or isobutyl chloride (3:7135) with excess ICl_3 in s.t. at 200° (129), from CaC_2 with gaseous or liq. Cl_2 at 20° under press. (10), from various iodochlorides of ethylene on warming (9), from lignin on boilg with $SbCl_5 + I_2$ (130), from humic acid with $KClO_3 + HCl$ (131), from β,β'-dichlorodiethyl sulfide ("mustard gas") with dry Cl_2 at 100° (132), or from $\alpha,\alpha,\beta,\beta,\beta,\beta'$-hexachlorodiethyl sulfide or $\alpha,\alpha,\beta,\beta,\beta,\alpha',\beta'$-heptachlorodiethyl sulfide with Cl_2 in cold (133) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis. [$\bar{C}$ passed over porcelain in hot tube gives (78) tetrachloroethylene (3:5460); $\bar{C}$ (in stream of air) pyrolyzed at 550–600° gives (57) tetrachloroethylene (3:5460) + CCl_4 (3:5100) in conversions of substantially 100%. — Note also that $\bar{C}$ with $SbCl_5$ above 450° yields almost exclusively (126) CCl_4 (3:5100).]

Reduction. $\bar{C}$ with granulated Zn in boilg. alc. (134), with Zn + dil. H_2SO_4 at room temp. for several days (100% yield (135)) (136) (76), with Zn + aq. above 80° (137), with H_2 over Ni at 270° (138), or with alc. KSH (139) loses 2 chlorine atoms giving tetrachloroethylene (3:5460) [for other, less direct conversions of $\bar{C}$ to tetrachloroethylene see latter under preparation; also below.)]

Oxidation. $\bar{C}$ is oxidized only with considerable difficulty [e g., for behavior of $\bar{C}$ over hot CuO see (140); for detn. of chlorine in $\bar{C}$ by cat. oxidn. over Fe_2O_3 (low results) see (141); $\bar{C}$ with CrO_3/H_2SO_4 is incompletely oxidized (142); $\bar{C}$ with SO_3 in s.t. at 150° (143) cf. (144) yields trichloroacetyl chloride + $S_2O_5Cl_2$.]

Partial replacement of chlorine by fluorine. [$\bar{C}$ with F_2 gas over Cu gauze cat. at 125° (145), or with SbF_3Cl_2 htd. under press. (146) (147) (148), or with $SbF_3 + Cl_2 + SbCl_3$ as directed (149) yields 1,1,2,2-tetrachloro-1,2-difluoromethane, m.p. 24–25°, b.p. 92°, accompanied by numerous other partially fluorinated prods.]

Behavior with alkalies. [$\bar{C}$ with solid KOH in s.t. at 210–220° for several days yields (150) KCl + potassium oxalate; $\bar{C}$ with alc. KOH in s.t. at 100° for a week yields (151) the same prods. accompanied by ethylene and hydrogen; $\bar{C}$ with $N/10$ abs EtOH/NaOH at 25° (17), with alc.-free NaOEt in ether under press. htd. to 140° (152), yields tetrachloroethylene (3:5460) (for study of kinetics see (17)).]

Behavior with metals. [$\bar{C}$ with alk. or alk.-earth metals is (like many other polychloro compounds) subject to explosion by mechanical shock; for study of sensitivity of $\bar{C}$ with Li, Na, K, Mg, Ca, Sr, Ba, Al, or Tl see (154). — $\bar{C}$ with "molecular" Ag at 280° loses 2 atoms of chlorine yielding (99) tetrachloroethylene (3:5460).]

Behavior with organometallic compounds. [For behavior of $\bar{C}$ with RMgX compds. see (155) (166); $\bar{C}$ does not (11) react with Hg di-(p-tolyl).]

Behavior with NH_3 or organic bases. [$\bar{C}$ with NH_3 at 700–800° gives up its halogen quant. (157) yielding NH_4Cl. — $\bar{C}$ with excess phenylhydrazine in xylene soln. on stdg or on warming is reduced to tetrachloroethylene (3:5460), HCl, C_6H_6, and N_2 also being formed (158) (note that analogous reactns. are also shown by 1,1,2,2-tetrachloroethane (3:5750) and by pentachloroethane (3:5880)). — For kinetics of reactn. of $\bar{C}$ with pyridine or piperidine see (159).]

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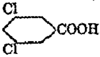
I 1716. (155) Korshak, *J. Gen. Chem. (U.S.S R)* **9**, 1153–1154 (1939); *C.A.* **34**, 1303 (1940). (156) Binaghi, *Gazz. chim. ital.* **57**, 674–675 (1927); *Cent.* **1928**, I 908; *C.A.* **22**, 573 (1928). (157) Heslinga, *Rec. trav. chim* **43**, 178–179 (1924). (158) Gowing-Scopes, *Analyst*, **39**, 385–386 (1914). (159) Tronow, *J. Russ. Phys.-Chem. Soc.* **58**, 1278–1301 (1926); *Cent.* **1927**, II 1145; not in *C.A.* (160) von Oettingen, *J. Ind. Hyg. Toxicol* **19**, 405 (1937).

(161) Rauscher, *Ind. Eng. Chem*, *Anal. Ed.* **9**, 296–299 (1937). (162) Schott, Schumacher, *Z. physik. Chem.* **B-49**, 107–125 (1941), *C.A.* **38**, 3551 (1944)

3:4840 3,5-DICHLOROBENZOIC ACID $C_7H_4O_2Cl_2$ Beil. IX - 344 IX$_1$-(141)



M.P. 188° (1) (2) (3) (4) (5)
184–185° (6)
182.5–183° (7) (11)
182–182.5° (8)

Ndls from alc. — Sublimes (10). — Very eas. sol. alc., spar. sol. aq. or lgr.

[For prepn from 3,5-dichlorotoluene (3:6310) by oxidn. with dil. HNO_3 at 150–170° see (8) (7); from 3,5-dichlorobenzaldehyde (3:1475) by oxidn with $KMnO_4$ (74% yield) see (3); from 3,5-dichlorobiphenyl (3:0360) by oxidn with CrO_3 + AcOH see (9): for prepn. from *3,5-diaminobenzoic ac.* via diazo reactn. see (1), from *4-amino-3,5-dichlorobenzoic ac.* via diazo reactn. see (2); from 3,5-dichloroaniline via conv. to acid hydrolysis of the nitrile see (10), for prepn. from 5-nitro-3-sulfobenzoic acid via PCl_5 and subsequent boilg. with alk. see (11).]

C̄ added to 8 pts. fumg. HNO_3 (D = 1.48), stood 2–3 hrs. at 70°, cooled, ppts. 75% yield 2-nitro-3,5-dichlorobenzoic ac., ndls. from dil. alc., m p 194° cor. (5). [This prod. depresses m.p. of C̄ (5).]

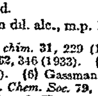
C̄ with PCl_5 yields (12) 3,5-dichlorobenzoyl chloride, b.p. 135–137° at 25 mm. (12).

—— **Methyl 3,5-dichlorobenzoate**: m p. 58° (13).
—— **Ethyl 3,5-dichlorobenzoate**: m.p. unrecorded. [For study of velocity of hydrolysis see (14).]
—— **3,5-Dichlorobenzamide**: unrecorded.
—— **3,5-Dichlorobenzanilide**: ndls. from dil. alc., m.p. 148° (15).

3:4840 (1) Bornwater, Holleman, *Rec. trav. chim.* **31**, 229 (1912). (2) Elion, *Rec. trav. chim.* **42**, 178 (1923). (3) Asinger, Lock, *Monatsh.* **62**, 346 (1933). (4) Lock, Böck, *Ber.* **70**, 923 (1937). (5) Asinger, *Monatsh.* **63**, 390–391 (1933/34). (6) Gassmann, Hartmann, *J. Am. Chem. Soc.* **63**, 2393–2395 (1941). (7) Cohen, Dakin, *J. Chem. Soc.* **79**, 1112, 1134 (1901). (8) Lellmann, Klotz, *Ann.* **231**, 324 (1885). (9) Hinkel, Hey, *J. Chem. Soc.* **1928**, 2789. (10) Claus, Stavenhagen, *Ann.* **269**, 225 (1892).

(11) Franchimont, *Rec. trav. chim.* **29**, 376 (1910). (12) Cohen, Briggs, *J. Chem. Soc.* **83**, 1214 (1903). (13) Müller, Tietz, *Ber* **74**, 807–824 (1941); *C.A.* **35**, 7953 (1941). (14) Blakey, McCombie, Scarborough, *J. Chem. Soc.* **1926**, 2863–2868. (15) Waters, *J. Chem. Soc.* **1929**, 2108.

3:4845 6-CHLORONAPHTHOIC ACID-1 $C_{11}H_7O_2Cl$ Beil. S.N. 951



M.P. **189° cor.** (4)
188–189° (1) (2)

Cryst. from C_6H_6 or 95% alc.

[For formn. of C̄ from furoic acid (1:0475) + chlorobenzene (3:7903) + $AlCl_3$ (18% yield (2)) (3) or from methyl furoate (1:3452) + chlorobenzene (3:7903) + $AlCl_3$ (yield 39% (1)) see indic. refs.]

C̄ on decarboxylation by htg. in quinoline at 225° in pres. of copper chromite cat. for 4 hrs. yields (2) 2-chloronaphthalene (3:1285), m.p. 58–59° (2).

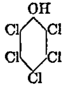
—— Methyl 6-chloro-1-naphthoate: b.p. 165–170° at 2 mm. (1). [From methyl furoate (1:3452) + chlorobenzene (3:7903) + $AlCl_3$ (15% yield (1)).]

—— Ethyl 6-chloro-1-naphthoate: unreported.

Ⓓ *p*-Bromophenacyl 6-chloro-1-naphthoate: m.p. 142–143° cor. (4).

3:4845 (1) Price, Huber, *J. Am. Chem. Soc.* **64**, 2139 (1942). (2) Price, Chapin, Goldman, Krebs, Shafer, *J. Am. Chem. Soc.* **63**, 1857, 1861 (1941). (3) McCorkle, Turck, *Proc. Iowa Acad. Sci.* **43**, 205–206 (1936), *Cent.* **1938**, II 1950; *C.A.* **32**, 4161 (1938). (4) Horn, Warren, *J. Chem. Soc.* **1946**, 144.

3:4850 PENTACHLOROPHENOL



C_6HOCl_5 — Beil. VI - 194; VI_1-(104); VI_2-(182)

M.P. 190.2° (1)	**B.P. 309–310° at 754.3 mm. sl. dec. (7)**
190–191° (2) (3) (4)	**195° at 16 mm. (3)**
189° (5)	
186–187° (8) (9) (10) (15)	

Cryst. from alc. as monohydrate, C̄.H_2O, m.p 174°; anhydrous ndls. from C_6H_6; sublimes in long ndls. — Very insol. aq. (17), very eas. sol. alc, ether; mod. sol. C_6H_6; spar. sol. cold lgr.; for quant data on solubility in 15 solvents at 7 temps. from 0° to 60° see (1) (17). — Odor pronounced only on htg ; dust of C̄ causes sneezing. — Slightly volatile with steam.

[For general review see (1), for use as wood preservative see (17) (19); for studies on toxicity see (20) (21); for fate of C̄ in organism see (22).]

[For prepn see Beil. VI-194, VI_1-(104); for comml. prepn. from hexachlorobenzene (3:4939) + NaOH + MeOH see (12) cf. (23); from chlorination of phenol or polychlorophenols in pres. of $AlCl_3$ see (13), from "hexachlorophenol" (3:3180) by reduction with SO_2 in alc. see (18).]

C̄ is acidic and in alc. soln titrates quant. using thymol-blue (Neut. Eq. = 266 5) (1). [For dissoc. const. see (2).] — C̄ is insol. in NH_4OH (1) but slowly dis. in cold Na_2CO_3 soln. (8) — C̄ in alk. soln. does not couple with diazonium salts. [For spectrophotometric detn. see (11).]

Salts. See Beil. VI-194. NaĀ, ndls. (from acetone + lgr.), spar. sol. aq. (3), NaĀ H_2O, loses aq. at 110°, sol. aq., alc., ether. [For comml. application as preservative see (1) (14).] — AgĀ, yel. ppt. turning orange on drying. — Heavy metal salts insol. aq. and often colored (1).

C̄ in alk. shaken with $(CH_3)_2SO_4$ (6), or C̄ treated with diazomethane (6), or C̄ htd. in MeOH with CH_3I + KOH (15), yields its methyl ether, pentachloroanisole, ndls. from alc., m.p. 108° (6), 106 5° (6).

Ⓓ Pentachlorophenyl acetate: from C̄ on htg with Ac_2O + NaOAc (15) or from C̄ in CS_2 + AcCl + $AlCl_3$ (16); ndls. from alc., m.p. 149.5–150 5° (16), 147–148° (15). [This prod. is very resistant to saponification (16).]

Ⓓ Pentachlorophenyl benzoate: from $\bar{C}$ + BzCl by warming in pyridine (3); ndls. from alc., m p. 164–165° (3), 150–160° (15), 159° (10). [Very resistant to saponification (16).]

–626 (1938). (2) Tiessens, *Rec. trav. chim* –4020 (1904). (4) Fels, *Z. Krist.* **32**, 369). (6) Pollak, Gebauer-Fülnegg, *Monatsh.* **20**, 545 (1890). (8) Merz, Weith, *Ber.* **5**,). (10) Brazier, McCombie, *J. Chem. Soc.*

11 (12) Smith, Livak (tc 32, 2548 (1938). (1 4312; *C.A.* **32**, 91 939; *Cent* **1939**, II (3) **13**, 342–343 (1 Britton, Alquist (to Dow Chem Co), U S 2,176,417, Oct 17, 1939, *C.A.* **34**, 1038 (1940). (19) Hatfield, *Proc. Am. Wood Preserving Assoc* **1944**, 4705, *C.A.* **39**, 2631 (1945). (20) Goodnight, *Ind. Eng. Chem* **34**, 868–872 (1942)

(21) Deichmann, Machle, Kitamiller, Thomas, *J. Pharmacol.* **76**, 104–117 (1942); *C.A.* **37**, 461 (1943). (22) Machle, Deichmann, Thomas, *J. Ind. Hyg. Toxicol.* **25**, 192–194 (1943). (23) Troitskii, Voronina, *Org. Chem. Ind. (U.S S.R.)* **7**, 240–241 (1940); *C.A.* **35**, 3989 (1941).

3:4853 CHLOROFUMARIC ACID

Cl—C—COOH
‖
HOOC—C—H

$C_4H_3O_4Cl$ Beil. II - 744
II_1-(302)
II_2-(640)

M.P.	193°	(1)
	192°	(2) (3) (4)
	191.5–192.5° cor.	(5)
	191.5°	(6)
	191–192°	(22)
	191°	(8) (10) (19)
	190–191°	(7) (12)
	189°	(11)
	188–189°	(14)

[*See also chloromaleic acid* (3 3432).]

Tbls from AcOH — $\bar{C}$ is very eas. sol. aq, alc. or ether; spar. sol. C_6H_6 or lgr. — $\bar{C}$ sublimes without forming anhydride

[For prepn of $\bar{C}$ from chloromaleic acid (3:3432) by repeated evapn. with conc. HCl see (5) (2); from *d,l-α,α'*-dichlorosuccinic acid (3:4711) on boilg. with aq (7), or with aq. KOH (8) (9) or aq acid (9) see indic refs; from *meso-α,α'*-dichlorosuccinic acid (3:4930) with aq KOH at 0° see (7) (8) (9) (note that from this source action of acid yields (9) both $\bar{C}$ and chloromaleic acid (3:3432)), from diethyl *d,l-α,α'*-dichlorosuccinate (3:9578) on hydrolysis with boilg 30% H_2SO_4 see (1); from diethyl chlorofumarate (3:6864) by evapn. with 1:1 HCl see (6); from chlorofumaro(di)nitrile (b p 172° at 74 mm., 64.0–64 2° at 10 mm., D_4^{20} = 1 2499, n_D^{20} = 1 49571 (22)), by hydrol. see (22).]

[For formn of $\bar{C}$ from diethyl oxaloacetate [Beil. III-782, III_1-(273), III_2-(479)] by actn. of PCl_5 followed by alc KOH see (11); from acetylenedicarboxylic acid [Beil. II-801, II_1-(317), II_2-(670)] with conc. HCl on stdg. 10 days at room temp. see (12) cf. (13); from 3-chlorofuroic acid [Beil XVIII-282] on oxidn with dil HNO_3 or from 3,5-dichlorofuroic acid [Beil. XVIII-283] or 4,5-dichlorofuroic acid [Beil. XVIII-283] on oxidn. with Br_2/aq. see (14).]

$\bar{C}$ on gentle boilg. largely decomposes into CO + CO_2 + HCl (5); but $\bar{C}$ on vigorous boilg. splits off aq. and isomerizes (or vice versa) yielding (5) chloromaleic anhydride (3:0280). — $\bar{C}$ with P_2O_5 (6) (15), or with $POCl_3$ (16) or with AcCl (5), gives on distn. chloromaleic anhydride (3:0280). — $\bar{C}$ (1 mole) with chlorofumaryl (di)chloride (3:6105) (1 mole) at 125° for 1 hr. also yields (17) chloromaleic anhydride (3:0280).

[$\bar{C}$ (as $K_2\bar{A}$) in aq. soln. with Na/Hg is dehalogenated and reduced yielding (18) succinic acid *(1:0530).*]

$\bar{C}$ readily reduces aq. $KMnO_4$.

[$\bar{C}$ in aq. soln. on protracted treatment with Cl_2 gives (19) β,β,β-trichloro-α,α-dihydroxypropionic acid ("trichloropyruvic acid hydrate") [Beil. III-623, III_1-(408)], ndls. from $CHCl_3$, m.p. 102° (19). — $\bar{C}$ does *not* (5) add Br_2 even at 100° (dif. from chloromaleic acid (3:3432)).]

$\bar{C}$ behaves normally as a dibasic acid: e.g., titration with standard dil. aq. alk. gives Neut. Eq. 75.3; for study of electrometric titration see (2).

[Salts. $(NH_4)_2\bar{A}$, cas. sol. aq. (5), but spar. sol. MeOH, EtOH, and insol. in ether, acetone, AcOEt, $CHCl_3$, or C_6H_6 (20) see indic. refs. — $KH\bar{A}$, much less sol. than corresp. prod. from chloromaleic acid, e.g., 100 g. of its satd. soln. at 15° conts. 3.843 g. $KH\bar{A}$ (5). — $Ag_2\bar{A}$ (10) (12). — $Ba\bar{A}.3H_2O$, fairly sol. aq. (10). — $Pb\bar{A}.2H_2O$ (13).]

[$\bar{C}$ on stdg. at ord. temp. with slight excess 0.76 N aq. KOH gives chlorine ion about 40 times as fast (12) as the isomeric chloromaleic acid (3:3432).]

The acid (di)chloride corresp. to $\bar{C}$, viz., chlorofumaryl (di)chloride (3:6105), has been reported only by indirect means.

—— Dimethyl chlorofumarate: oil (see 3:6582).

—— Diethyl chlorofumarate: oil (see 3:6864).

Ⓓ *bis*-(*p*-Nitrobenzyl) chlorofumarate: m.p. 138.5° (21). [From $Na_2\bar{A}$ with *p*-nitrobenzyl bromide in 63% alc. refluxed 2 hrs. (21).]

—— Chloromaleanil [*N*-phenyl-chloromaleinimide]: ndls. from boilg. alc., m.p. 170° (17). [From aniline salt of $\bar{C}$ on htg. for a few minutes at 170°–180°; note that during the process isomerization occurs and therefore that the prod. is the same as similarly obtd. from chloromaleic acid (3:3432) q.v.]

Ⓓ Chlorofumaro-*bis*-(*p*-chloroanilide): pale yel. ndls. from alc., m.p. 223° (17). [From chlorofumaryl (di)chloride (3:6105) with *p*-chloroaniline (4 moles) in dry ether; note that crude prod. is also accompanied by a little *N*-(*p*-chlorophenyl)-chloromaleinimide, m.p. 175° (17).]

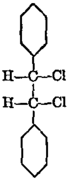
Ⓓ Chlorofumaro-*bis*-(*p*-bromoanilide): faintly yel. ndls. from boilg. alc., m.p. 236° (17). [From chlorofumaryl (di)chloride (3:6105) with *p*-bromoaniline (4 moles) in dry ether; note that crude prod. is also accompanied by a little *N*-(*p*-bromophenyl)-chloromaleinimide, m.p. 190° (17).]

3:4853 (1) Patterson, Todd, *J. Chem. Soc.* **1929**, 1769, 1770. (2) Ashton, Partington, *Trans. Faraday Soc.* **30**, 602, 605–606, 608 (1934). (3) Langseth, *Z. physik. Chem.* **118**, 54 (1925). (4) Stelling, *Z. physik. Chem.* **B-24**, 410, 424 (1934). (5) Perkin, *J. Chem. Soc.* **53**, 697–700, 703–705 (1888). (6) von Auwers, Harres, *Ber.* **62**, 1685–1687 (1929). (7) Michael, Tissot, *J. prakt. Chem.* (2) **46**, 393–395 (1892). (8) Robinson, Lewis, *J. Chem. Soc.* **1933**, 1260. (9) Holmberg, *Arkiv Kemi, Mineral., Geol.* 8, No. 2, 33 (1920); *Cent.* **1921**, I 830; *C.A.* **16**, 2116 (1922). (10) Kauder, *J. prakt. Chem.* (2) **31**, 29–32 (1885).

(11) Nef, *Ann.* **276**, 223–226 (1893). (12) Michael, *J. prakt. Chem.* (2) **52**, 306–308, 321–322 (1895). (13) Bandrowski, *Ber.* **15**, 2695 (1882). (14) Hill, Jackson, *Am. Chem. J.* **12**, 36, 50, 115 (1890). (15) Walden, *Ber.* **30**, 2885–2886 (1897). (16) Thomas-Mamert, *Bull. soc. chim.* (3) **13**, 847 (1895). (17) Chattaway, Parkes, *J. Chem. Soc.* **125**, 466 (1924). (18) Perkin, *Ann.* **129**, 373–374 (1864). (19) Buchner, *Ber.* **26**, 656–657 (1893). (20) McMaster, Magill, *J. Am. Chem. Soc.* **38**, 1802–1803 (1916).

(21) Lyons, Reid, *J. Am. Chem. Soc.* **39**, 1733 (1917). (22) Mommaerts, *Bull. classe sci., Acad. roy. Belg.* (5) **27**, 579–597 (1941); *Cent.* **1943**, I 615–616; *C.A.* **38**, 3621 (1944).

3:4854 *meso*-**1,2-DICHLORO-1,2-DIPHENYLETHANE** (*meso*-α,α'-Dichlorobibenzyl; "α"-stilbene dichloride)



$C_{14}H_{12}Cl_2$

Beil. V - 600
V_1-(281)
V_2-(507)

M.P. [194.5–195.5° cor.	(1) (15)]
193–194°	(25)
193°	(2) (6)
192.4–193.4° cor.	(3)
192–193°	(8) (19) (22)
192°	(4) (5) (6)
191–193°	(7) (17)
191–192°	(16), u.c. (15)
190–192°	(21)
191°	(9) (10)
190.5–191°	(11)
190°	(12) (13)
189–190°	(14)
188–189°	(20)

[*See also the isomeric d,l or "β"-stilbene dichloride* (3:2570).]

Colorless ndls. from alc., AcOH, C_6H_6, toluene, or lgr. — Spar. sol. hot alc., eas. sol. hot toluene. — Sublimes.

PREPARATION OF $\bar{C}$

From Binuclear Initial Materials

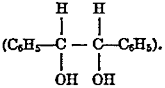
From stilbene (*trans*-1,2-diphenylethylene). [For prepn. of $\bar{C}$ from 1,2-diphenylethylene (stilbene) (1:7250) with Cl_2 in $CHCl_3$ (8) (16), with Cl_2 in ether in sunlight (17) (some "β"-stilbene dichloride (3:2570) is also formed), with Cl_2 in ethane soln. (note low temp.) *in sunlight (gives 34 4% yield* $\bar{C}$ + *48.7% yield diastereomer (3:2570)* (15)) see indic. refs.; with PCl_5 (2 moles) in $CHCl_3$ soln. (6) or with PCl_5 in $POCl_3$ in s.t. at 170° (2) see indic. refs.; with SO_2Cl_2 in presence of peroxides at room temp. (yield of crude mixt. is 100%; sepn. of isomers gives 45% $\bar{C}$ + 33% diastereomer (3:2570) (7)), with nitryl chloride ($ClNO_2$) in ether (57% yield (18)), see indic. refs.]

From isostilbene (*cis*-1,2-diphenylethylene). [For prepn. of $\bar{C}$ from isostilbene with PCl_5 in C_6H_6 stood 2 days at room temp. see (6).]

From bibenzyl. [For formn. of $\bar{C}$ from bibenzyl (1:7149) with chromyl chloride (CrO_2Cl_2) in CS_2 (other prods. are also formed) see (19).]

From α,α'-dibromobibenzyl (stilbene dibromide). [For formn. of $\bar{C}$ from the higher-melting *diastereomer* (*m* p. 236°) of stilbene dibromide [Beil. V-602, V_1-(282), V_2-(508)] with $SnCl_4$ in C_6H_6 on refluxing ½ hr. (5) (note that at ord. temp. replacement is only

partial and yields (5) only stilbene chlorobromide, m.p. 225°) or with $HgCl_2$ in acetone/$CHCl_3$ refluxed 11 hrs. (poor yield (11)) see indic. refs.]

From α,α'-dihydroxybibenzyl .

From meso-hydrobenzoin. [For prepn. of $\bar{C}$ from *meso*-hydrobenzoin [Beil. VI-1003, VI_1-(490)] with PCl_5 (2 moles) (20) cf. (15) (yield 43% $\bar{C}$ + 22% diastereomer (3:2570) (8) (16)), with PCl_3 (8) (16), or with $SOCl_2$ in C_6H_6 + pyridine (100% yield (10)) (13) see indic. refs.]

From d,l-hydrobenzoin (isohydrobenzoin). [For prepn. of $\bar{C}$ from isohydrobenzoin [Beil. VI-1004, VI_1-(490)] with PCl_5 (27–32% $\bar{C}$ + much resin (8)) (16) (20) or with PCl_3 (8) (16) see indic. refs.; note, also, that *l*-isohydrobenzoin with PCl_5 in $CHCl_3$ refluxed 2 hrs. gives (45% yield (1)) $\bar{C}$.]

From α-chloro-α'-hydroxybibenzyl. [For formn. of $\bar{C}$ from α-chloro-α'-hydroxybibenzyl (m.p. 77°, corresp. *p*-nitrobenzoate, m.p. 103–104° (3)) with $SOCl_2$ in $CHCl_3$ see (3); note that by this method $\bar{C}$ is formed exclusively.]

From α-amino-α'-hydroxybibenzyl. [For prepn. of $\bar{C}$ from *d,l*-α-amino-α'-hydroxybibenzyl with PCl_5 (42% yield (21)) or with NOCl (1) see indic. refs.; note also that *d*-α-amino-α'-hydroxybibenzyl in HCl with NOCl gives (1) 13% $\bar{C}$ + 24% of *l*-"β"-stilbene dichloride (3:2570) while *l*-α-amino-α'-hydroxybibenzyl in HCl with NOCl gives (1) 14% $\bar{C}$ + 17% *d*-"β"-stilbene dichloride (3:2570).]

From Mononuclear Initial Materials

From benzal (di)chloride. [For formn. of $\bar{C}$ from benzal (di)chloride (3:6327) by bimolecular reduction with H_2 + Pd in alc. soln. (22), or with H_2 + hydrazine hydrate in MeOH/KOH (20% yield (12)), or with excess conc. (2 molar) MeMgI in ether refluxed 2 hrs. (22% yield (14)), or with excess C_6H_5MgBr similarly (14), or by action of Ni on htg. in CO_2 (23), see indic. refs.]

From benzotrichloride. [For formn. of $\bar{C}$ from benzotrichloride (3:6540) by actn. of Ni on htg. in atm. of CO_2 see (23).]

From Miscellaneous Initial Materials

[For formn. of $\bar{C}$ from diphenylacetaldehyde [Beil. VII-438, VII_1-(234)] with PCl_5 in C_6H_6 under reflux 2 hrs. (41% yield) see (3).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Action of heat. $\bar{C}$ on repeated htg. above its m.p. is partially isomerized to its diastereoisomer (3:2570) as a result of which the m.p. of the sample gradually falls to about 160° but not lower (8) (16).

Reduction. $\bar{C}$ with Zn dust + AcOH gives good yields (24) of *trans*-1,2-diphenylethylene (stilbene) (1:7250), m.p. 124°.

Hydrolysis. [No study of the direct hydrolysis of $\bar{C}$ appears to be recorded. — However, $\bar{C}$ with AgOAc in boilg. AcOH gives an ester which upon hydrolysis gives (60% yield (8) (16)) almost exclusively *d,l*-hydrobenzoin (isohydrobenzoin), accompanied by a little

hydrobenzoin; with AgOBz, however, much more of the latter results; however, see also below.]

Other reactions. C̄ with alc. KOH on warming under reflux (20) or in an autoclave at 180° (2) splits out 2 HCl yielding diphenylacetylene (tolane) [Beil. V-656, V_1-(319), V_2-(568)], m p 60°. — C̄ with pyridine in s.t. at 200° for 8 hrs. does *not* (17) split out HCl (dif. from the "β" stereoisomer (3·2570) q v.)

[C̄ with LiI in alc. refluxed 2 hrs. is little affected but in s.t. at 200° for 3 hrs. gives (11) (presumably via halogen interchange and subsequent loss of I_2) a little *trans*-1,2-diphenylethylene (stilbene) (1:7250). — C̄ with NaI in alc. is unchanged even at 150° in s.t.; using AcOH as solvent, however, in s t. at 210° stilbene (1:7250) is formed (11). — C̄ does not (11) react with alc. NaBr.]

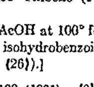
[C̄ with AgOAc (2 moles + 25% excess) in AcOH at 100° for 9 hrs. gives (25) mixts. of hydrobenzoin diacetate, m.p. 133–134°, and isohydrobenzoin diacetate, m.p. 114–116° (for m.p./compn. diagram of this pair see (25) (26)).]

3:4854 (1) Weissberger, Bach, *Ber* **64**, 1095–1108 (1931). (2) Kayser, *Ann. chim.* (11) **6**, 220–222 (1936). (3) Newman, Joshel, Wise, *J. Am. Chem. Soc.* **62**, 1862 (1940). (4) Reulos, *Compt. rend.* **216**, 775–776 (1943). (5) Pfeiffer, Eistert, *J. prakt. Chem* (2) **124**, 174–175 (1930). (6) Bergmann, Bondi, *Ber.* **64**, 1457–1458, 1468 (1931). (7) Kharasch, Brown, *J. Am. Chem. Soc* **61**, 3434 (1939) (8) Zincke, *Ann.* **198**, 120–141 (1879). (9) Higasi, *Bull. Chem. Soc. Japan*, **13**, 159 (1938). (10) Kitasato, Sone, *Ber.* **64**, 1144 (1931).

(11) Pfeiffer, Praetorius, *J prakt. Chem* (2) **137**, 30–31, 37–39 (1933). (12) Busch, Weber, *J. prakt Chem* (2) **146**, 49–50 (1936). (13) Carré, Mauclere, *Compt rend.* **192**, 1568–1569 (1931). (14) Fuson, Ross, *J Am. Chem Soc* **55**, 720–723 (1933). (15) Weissberger, Sängewald, *Z. physik. Chem.* **B-9**, 140 (1930). (16) Zincke, *Ber* **10**, 999–1004 (1877) (17) Pfeiffer, *Ber.* **45**, 1816–1817 (1912). (18) Steinkopf, Kühnel, *Ber* **75**, 1327 (1942). (19) Weiler, *Ber.* **32**, 1054 (1899). (20) Fittig, Ammann, *Ann* **168**, 73–74, 77–78 (1873).

(21) Darapsky, Spannagel, *J. prakt. Chem.* (2) **92**, 293 (1915). (22) Borsche, Heimburger, *Ber* **48**, 457 (1915). (23) Korczynski, Reinholz, Schmidt, *Roczniki Chem.* **9**, 731–740 (1929); *Cent.* **1930**, I 2075, *C A.* **24**, 1858 (1930) (24) Meisenheimer, Heim, *Ann* **356**, 274 (1907). (25) Winstein, Seymour, *J. Am. Chem. Soc.* **68**, 119–122 (1946) (26) Böeseken, Elsen, *Rec. trav. chim.* **47**, 696 (1928).

3:4855 5-CHLOROBENZENETRICARBOXYLIC ACID-1,2,4 $C_9H_5O_6Cl$ Beil. S.N. 1008
(5-Chlorotrimellitic acid)



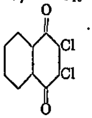
M.P. 192–194° (1)

[For prepn. of C̄ from 5-chloro-1,2,4-trimethylbenzene (5-chloropseudocumene) [Beil. V-402] by oxidn. in aq. pyridine with $KMnO_4$ see (1).]

[C̄ on suitable treatment with alk. yields (1) 5-hydroxytrimellitic acid [Beil. X-580] for use as dye intermediate.]

3:4855 (1) I.G., Brit. 495,432, Dec. 8, 1938; *Cent.* **1939**, I 1452; *C.A.* **33**, 2913 (1939); French 839,454, April 4, 1939, *C.A.* **36**, 5188 (1942).

3:4857 2,3-DICHLORONAPHTHOQUINONE-1,4 $C_{10}H_4O_2Cl_2$ Beil. VII - 729 VII_1-(386)



M.P.	**196°**	(1)
	193°	(2) (3)
	192.5° cor.	(4)
	192°	(5)
	190° cor.	(6)
	189–192°	(7)
	189–190°	(8)
	189° u.c.	(9)
	189°	(10) (11)
	188.5° u.c.	(4)
	188°	(20)
	186°	(12)

Golden yellow ndls. from AcOH (contg. a little CrO_3 (2)) or from alc. — Sublimes (use in purification (12)). — Insol. aq. (1 in 10,000,000 (13)), spar. sol. cold alc AcOH, CCl_4, ethyleneglycol ethyl ether, gasoline, cottonseed oil, castor oil, "Nujol" (13); quite sol. (4% (13)) in xylene or *o*-dichlorobenzene (3:6055); fairly sol. in ether, C_6H_6, acetone, or dioxane (13).

[For use of $\bar{C}$ as agricultural and textile fungicide see impt. review article (13) cf. (37).]

[For prepn. of $\bar{C}$ from naphthoquinone-1,4 (1:9040) in AcOH with Cl_2 in pres. of I_2 (yields: 90% (14), 80% (8)), from 2-chloronaphthoquinone-1,4 [Beil. VII-729] in AcOH with Cl_2 (15) (16), from naphthoquinone-1,4-*N*-chloromonimide [Beil. VII-726] in AcOH with 8–10 pts. conc. HCl on warming (70% yield (11)) see indic. refs.; from naphthol-1 (1:1500) with HCl + $KClO_3$ (6) or after preliminary sulfonation to naphthol-1-sulfonic acid-4 (Neville-Winther acid) followed by HCl + $KClO_3$ (yields: 83% crude (4), 47% (2), 40–47% (12)) (17) (18), from 4-nitrosonaphthol-1 (naphthoquinone-1,4-monoxime) [Beil. VII-727, VII_1-(386)] in ether with HCl gas (3), from 4-aminonaphthol-1 in AcOH with Cl_2 (17), from 2,3-dichloronaphthol-1 (3:2935) in AcOH with CrO_3 (19), or from 2,4-dinitrophenol (Martius Yellow) [Beil. VI-617, VI_1-(308)] with HCl + $KClO_3$ (24% yield (2)) (10) see indic. refs.]

[For formn. of $\bar{C}$ from 1,4-dihydroxynaphthalene-3-pyridinium chloride (itself from naphthoquinone-1,4 (1:9040) + pyridine in MeOH + HCl) with $SOCl_2$ under reflux see (7); from naphthalene (1:7200) in AcOH with CrO_2Cl_2 see (20); from 1,2,3,4-tetrachloronaphthalene [Beil. V-546, V_2-(446)] in AcOH with CrO_3 or with conc. HNO_3 in s.t. at 110° see (9); from naphthalene tetrachloride-1,2,3,4 (3:4750) with conc. HNO_3 see (1): from 2,2,3,4,4,-pentachloro-1-oxo-naphthalene tetrahydride [Beil. VII-370] with dil. alc. or dil. AcOH in s.t. at 120–130° see (15).]

[$\bar{C}$ on reduction by shaking ether soln. with aq. $SnCl_2$ (21), or with Sn + HCl (part of halogen is lost (10)), or by refluxing with HI + white P (10) gives 2,3-dichloro-1,4-dihydroxynaphthalene [Beil. VI-979], colorless scales from alc., m.p. 135° (21), 135–140° (10); note that $\bar{C}$ is reduced by SO_2 + aq. only in s.t. at 130–140° (10). — Note that $\bar{C}$ with aq. K_2SO_3 or aq. $KHSO_3$ soln. replaces both chlorine atoms giving (10) K salt of 4-hydroxy-2,3-disulfonaphthyl-1 sulfuric acid [Beil. XI-304].]

$\bar{C}$ on oxidn. with boilg. HNO_3 (D = 1.35) slowly yields (10) phthalic acid (1:0820).— $\bar{C}$ with aqua regia htd. in s.t. yields (22) phthalic (or nitrophthalic) acid accompanied by some trichloronaphthoquinone-1,4 [*Beil. VII-730*], *yel. ndls.*, m.p. 250°.

$\bar{C}$ with equal wt MnO_2 + 4 8 wts conc. HCl in s.t. at 230° for 10 hrs. (11) cf. (17) yields 2,2,3,3-tetrachloro-1,4-dioxonaphthalene tetrahydride-1,2,3,4 [Beil. VII-702], colorless pr. from ether, m.p 117° (11).

$\bar{C}$ with PCl_5 (2 moles) dislvd. in $POCl_3$ htd. in s.t. at 180–200° (10), or at 200–250° for 4–5 *hrs* (22) (*with slow rise of temp. to avoid explosion*), *yields* 1,2,3,4,5-pentachloronaphthalene [Beil. V-546], colorless ndls. from alc , m p 168 5° (10) (22).

[$\bar{C}$ with large excess MeMgI in ether gives (45% yield (23)) (by replacement of 1 atom of chlorine and usual reactn. of the two carbonyl groups) 1,2,4-trimethyl-1,4-dihydroxy-3-chloro-1,4-dihydronaphthalene, cryst. from ether by pptn with pet. ether, m.p. 115–117° (23); with certain other RMgX cpds , however, *both* chlorine atoms are replaced, e g., $\bar{C}$ with large excess C_6H_5MgBr in ether gives (34% yield (23)) 1,2,3,4-tetraphenyl-1,4-dihydroxy-1,4-dihydronaphthalene, cryst. from C_6H_6 + alc , m.p. 241.5° (23); with still other RMgX cpds. *neither halogen is affected and only the carbonyl groups react*; e g , $\bar{C}$ with large excess α-$C_{10}H_7MgBr$ in ether gives (75% yield (23)) 1,4-di-α-naphthyl-1,4-dihydroxy-2,3-dichloro-1,4-dihydronaphthalene, m.p. 261° dec. (23).]

[$\bar{C}$ with 2 pts. Cu powder htd. in nitrobenzene or at 240° as directed (24) gives 3% yield triphthaloylbenzene (1,2,3,4-diphthaloylanthraquinone). — $\bar{C}$ with HBr in nitrobenzene htd in pres. of $CuCl_2$ yields (25) 2-bromo-3-chloronaphthoquinone-1,4, m p. 206–207° (25)]

[$\bar{C}$ with 2,3-dimethylbutadiene-1,3 (1:8050) in pres. of excess 5% alc KOH and a little sodium hydrosulfite boiled 2 hrs. and then oxidized with air gives (26) 2,3-dimethylanthraquinone [Beil. VII-815, VII_1-(425)], *yel. ndls from alc., m.p. 205–206°.*]

$\bar{C}$ with boilg alc. KOH hydrolyzes 1 chlorine yielding on acidification (10) 3-chloro-2-hydroxynaphthoquinone-1,4 [Beil. VIII-304], yel ndls. from alc., m.p. 215°; note that $\bar{C}$ with NaOAc htd in alc. yields (27) the corresp acetate, viz., 3-chloro-2-acetoxynaphthoquinone-1,4, yel. ndls from hot alc., m.p. 98° (27). — [For reactn. of $\bar{C}$ with Na_2S or with H_2S leading to bimolecular condensation with formn. of dibenzothianthrene diquinone or its derivs. see (28) (8).]

$\bar{C}$ with phenol (2 moles) + dry K_2CO_3 (i.e , K phenolate) htd. for 1 hr. at 100° gives (96% *yield* (2)) *2,3-diphenoxynaphthoquinone-1,4, or.-yel. ndls. from xylene,* m.p. 205° (2) — [For reactn of $\bar{C}$ with pyrocatechol (1:1520) in pres. of diethylaniline (2), with pyrogallol (1 1555) in pres of pyridine (29), or with various anthrols and pyridine in *prepn. of vat dyes (30) see indic. refs*]

$\bar{C}$ in nitrobenzene treated with NH_3 gas or $\bar{C}$ in boilg. alc. treated dropwise with conc. NH_4OH (27) gives (probably by 1,4-addition and subsequent loss of 1 HCl (31)) (80% yield (2)) 3-chloro-2-aminonaphthoquinone-1,4, yel -br. ndls. from AcOH, m.p. 193° (2) (corresp acetyl deriv., m p. 219° (27)). — Similarly, $\bar{C}$ with aniline (2 moles) in hot alc. gives (87% *yield* (12)) (32) *3-chloro-2-anilinonaphthoquinone-1,4* [*Beil. XIV-168*, XIV_1-(434)], copper-red ndls , m p 202° (32). — [For corresp. reactn. of $\bar{C}$ with many other aliphatic or arom amines see (33), with β-naphthylamine see (34), with p-phenylenediamine (or its monoacetyl deriv) see (12); with p-chloroaniline see (27); note that some amines, e g , o-nitroaniline, 2-aminoanthraquinone, and 3-chloro-2-aminonaphthoquinone do *not* undergo this reactn. (27) — For reactn. of $\bar{C}$ with pyridine see (2).]

$\bar{C}$ on nitration, e g , with 4 vol/pts red fumg HNO_3 (D = 1.52) + 2½ vol/pts. pure conc. H_2SO_4 at 100° for 6 hrs. (35) cf (36), gives (40–45% yield (35)) 5-nitro-2,3-dichloronaphthoquinone-1,4, pale yel. cryst. from $CHCl_3$ (35), AcOH (36), or alc. (36), m p. 175° (35) (36); this prod. with aniline (2 moles) in hot alc. yields (35) 3-chloro-2-anilino-5 (8)-nitronaphthoquinone-1,4, lfts. from nitrobenzene, m p. 273° (35).

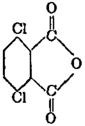
3:4857 (1) Helbig, *Ber.* **28**, 505–506 (1895). (2) Ullmann, Ettisch, *Ber.* **54**, 259–272 (1921). (3) Angeletti, Pirona, *Atti accad. Torino, Classe sci. fis., mat. nat.* **71**, 602–606 (1926); *Cent.* **1937**, I 1138; *C.A.* **31**, 678 (1937). (4) Conant, Fieser, *J. Am. Chem. Soc.* **46**, 1873, 1875 (1927). (5) Liebermann, *Ber.* **32**, 264 (1899). (6) Darmstädter, Wichelhaus, *Ann.* **152**, 301 (1869). (7) Koenigs, Greiner, *Ber.* **64**, 1047 (1931). (8) Brass, Köhler, *Ber.* **55**, 2554 (1922). (9) Claus, Mielcke, *Ber.* **19**, 1184–1185 (1886). (10) Graebe, *Ann.* **149**, 3–12 (1869).

(11) Friedlander, Reinhardt, *Ber.* **27**, 240 (1894). (12) Fries, Kerkow, *Ann.* **427**, 286–287, 295–296 (1922). (13) Ter Horst, Felix, *Ind. Eng. Chem.* **35**, 1255–1259 (1943). (14) Bertheim, *Ber.* **34**, 1554 (1901). (15) Zincke, Kegel, *Ber.* **21**, 1039, 1045 (1888). (16) Zincke, Schmidt, *Ber.* **27**, 2757 (1894). (17) Zincke, Cooksey, *Ann.* **255**, 370, 372 (1889). (18) Kehrmann, *Ber.* **21**, 1780 (1888). (19) Claus, Knyrim, *Ber.* **18**, 2928–2929 (1885). (20) Carstanjen, *Ber.* **2**, 633 (1869).

(21) Claus, *Ber.* **19**, 1142, 1144 (1886). (22) Claus, von den Lippe, *Ber.* **16**, 1016–1017 (1883). (23) Clar, Engler, *Ber.* **64**, 1597–1602 (1931). (24) Scholl, Wanka, Dehnert, *Ber.* **69**, 2433 (1936). (25) I.G., Ger. 597,259, May 25, 1934; *Cent.* **1934**, II 1688. (26) I.G., French 37,684, Jan. 14, 1931; *Cent.* **1931**, I 124. (27) Fries, Ochwat, *Ber.* **56**, 1295–1300 (1923). (28) Brass, Köhler, *Ber.* **54**, 594–597 (1921). (29) Ghosh, *J. Chem. Soc.* **107**, 1595 (1915). (30) I.G., Brit. 300,407, Dec. 6, 1928, *Cent.* **1929**, I 1622.

(31) Lindemann, Pabst, *Ann.* **462**, 37 (1928). (32) Knapp, Schultz, *Ann.* **210**, 189–190 (1881). (33) Plagemann, *Ber.* **15**, 484–488 (1882). (34) Fries, Köhler, *Ber.* **57**, 509 (1924). (35) Fries, Pense, Peeters, *Ber.* **61**, 1401 (1928). (36) Stock (to I. G.), Ger. 468,507, Nov. 15, 1928; Brit. 288,927, May 10, 1929; French 643,447, Sept. 17, 1928; *Cent.* **1929**, II 96. (37) Ter Horst (to U.S. Rubber Co.), U.S. 2,349,771–2, May 23, 1944; *C.A.* **39**, 1246 (1945).

3:4860 3,6-DICHLOROPHTHALIC ANHYDRIDE



$C_8H_2O_3Cl_2$ Beil. XVII - 483
XVII$_1$-(254)

M.P.	**193.5–194.5°** cor.	(1)
	191° cor.	(2)
	190–191°	(3)
	187°	(4)
	184–186°	(5)
	185°	(6) (7)

B.P. **339°** (3)

[*See also* 3,6-*dichlorophthalic acid* (3:4870).]

Long colorless ndls. — Sublimes.

[For prepn. of C̄ from 3,6-dichlorophthalic acid (3:4870) by htg. at 130–140° (2) (3) (4), at 160° (8), at 180–190° (5), by distn. under diminished press. (9), or by htg. in a current of dry air at 40° (?) (10) see indic. refs.: from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200–220° see (2) (5): for formn. of C̄ (together with other isomers) from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe or Fe salts at 160–260° (11) or with Cl_2 in fumg H_2SO_4 (12) in pres. of I_2 (3), or from 3-chlorophthalic anhydride (3:3900) with Cl_2 in fumg. H_2SO_4 in pres. of I_2 (3), see indic. refs.]

[For sepn. of C̄ from isomeric dichlorophthalic anhydrides by means of salts of corresp. acids, etc., see (3) (13) (1); by means of differential hydrolysis with H_2SO_4 (prods. with no α-chlorine such as 4,5-dichlorophthalic anhydride require H_2SO_4 of 98–100% concn., those with 1 α-chlorine such as 3,4-dichlorophthalic anhydride hydrolyze with 56–95% H_2SO_4, those with 2 α-chlorine atoms such as C̄ or 3,4,5,6-tetrachlorophthalic anhydride hydrolyze at H_2SO_4 concns. of less than 50%) see (14).]

C̄ dislvd. in abs. EtOH yields the acid ester, viz., ethyl hydrogen 3,6-dichlorophthalate,

cryst. from CCl_4, m p 130–131° (3), 128–130° (2), 128–129° (5); note that this ester when dislvd. in EtOH and satd with HCl gas, then warmed, does *not* convert to the neutral ester readily, and that even with 15 pts. EtOH and 7 hr. htg. only 16% diethyl 3,6-dichlorophthalate is formed (2)

[C̄ with 1 mole PCl_5 htd in s t. at 160° for 6–7 hrs. (8) or at 200° for 6 hrs. (15) yields *pseudo*-3,6-dichlorophthaloyl dichloride (3,3,4,7-tetrachlorophthalide), cryst. from C_6H_6, m p. 122° (15), this prod upon htg above its m.p , or upon solution in inert solvents, or very rapidly upon treatment of such solns. with decolorizing carbon, or slowly even in solid condition, isomerizes to *sym*-3,6-dichlorophthaloyl dichloride, colorless pr., m.p. 31° (15), from low-boilg pet ether (in which the *pseudo*-chloride is spar. sol.). — With MeOH the *pseudo* chloride yields the *pseudo* dimethyl ester (4,7-dichloro-3,3-dimethoxyphthalide, m p 134° (15); the neutral dimethyl 3,6-dichlorophthalate (corresp to the *sym.*-chloride) has m p 82° (15)] — [C̄ with 2 moles PCl_5 htd in s t several hrs at 200° is claimed (8) to yield a prod $C_8H_2OCl_6$, ndls. from alc , m p 117° (8)]

[C̄ with 1 mole $NH_2OH\,HCl$ + Na_2CO_3 in aq. as directed (3) for 3,4-dichlorophthalic anhydride (3:4880) yields 3,6-dichlorophthalylhydroxylamine (*N*-hydroxy-3,6-dichlorophthalimide) [Beil. XXI-504], ndls from MeOH, m p. 253–258° (3); the conv. of this prod. with boilg aq Na_2CO_3 to 3,6-dichloroanthranilic acid (analogous to the corresp. process with its isomers) has not been reported (see, however, under the imide below).]

[C̄ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (16) 2,5-dichlorobenzoic acid (3 4340).]

C̄ with $AlCl_3$ + C_6H_6 yields (8) (17) 3,6-dichloro-2-benzoylbenzoic acid [Beil. X-750, X_1-(357)], ndls from C_6H_6 (17) or dil alc (8), m.p. 168.5° (18), cor (17), 159° (8); this prod. on ring closure by htg. with conc H_2SO_4 (2) (17) (18) (19) yields 1,4-dichloroanthraquinone [Beil. VII_1-(411)], yel. ndls. from AcOH, m p. 187 5–188° (20), 187 5° cor. (17), 187.5° (18), 186° (19). — [For corresp. reactns of C̄ + $AlCl_3$ with chlorobenzene (22), with toluene (21), with *o*-chlorotoluene (3:8245) (23), with *p*-chlorotoluene (3:8287) (24), with fluorene (25), with acenaphthene (26), with pyrene (27), or with β-methylbenzanthrone (28) see indic refs.]

[C̄ with hydroquinone (1:1590) + H_3BO_3 htd. at 190° and afterward treated with hot conc. H_2SO_4 (29), or htd. with $AlCl_3$ + NaCl at 200–220° for 20 min (30), gives (yield: 30% (29), 84% (30)) 5,8-dichloro-1,4-dihydroxyanthraquinone (5,8-dichloroquinizarin) [Beil $VIII_1$-(715)], cryst from xylene (30) or AcOH (29), m p 275 5° (30), 266° (29) (diacetate, m p 180° (30), 170° (29))] — [For reactn of C̄ with $AlCl_3$ + *o*-cresol (31), with *o*-cresol methyl ether (31) (19), or with *p*-cresol (7) see indic refs.; for reactn. of C̄ with α-naphthol + H_3BO_3 see (9)]

[C̄ in fumg H_2SO_4 treated with Br_2 yields (33) (34) 3,6-dichloro-4,5-dibromophthalic anhydride, colorless ndls. from AcOH, m p 269–270° (34), 261° (33). — C̄ in fumg H_2SO_4 (50% SO_3) htd with I_2 as directed (32) gives (97% yield) 3,6-dichloro-4,5-di-iodophthalic anhydride, yel pr from AcOH, m p. 258°–258 5° cor. (32)]

[For condens of C̄ with substituted *m*-aminophenols in prepn. of phthalein dyestuffs see (35); for use of C̄ in prepn. of pigments of phthalocyanine type see (36) (37); for use of C̄ as plasticizer for cellulose esters see (38).]

Fused C̄ treated with dry NH_3 gas (39) or with urea (37) yields 3,6-dichlorophthalimide [Beil. XXI-504], ndls from alc., m p 242° (39) [This prod on ring opening and Hofmann degradation with aq alk NaOCl (3) or NaOBr (39) gives 3,6-dichloroanthranilic acid [Beil. XIV-367], ndls from aq or AcOH, m p 153° cf. (3). — [For behavior of C̄ with hydrazine hydrate yielding acc. to conditions *N*-amino-3,6-dichlorophthalimide, *N*-(3,6-dichlorophthalimido)-3,6-dichlorophthalimide, or 3,6-dichlorocyclophthalhydrazide see (40)]

$\bar{C}$ (1 pt.) dislvd. in 5 pts. boilg. AcOH and treated with 1 pt. aniline gives on cooling (82% yield (1)) 3,6-dichlorophthalanil [Beil. XXI_1-(391)], pale yel. lfts., or ndls. from AcOH, m.p. 201° (10), 197–198° cor. (1), 194° (41), 191° (39). [Note, however, that on protracted htg. with excess aniline first one and then the other nuclear halogen also reacts yielding, respectively, 3-anilino-6-chlorophthalanil, unstable form, m p. 141° cor. (1), stable form., m.p. 160–160.5° cor. (1), and 3,6-dianilinophthalanil, m.p. 197° (41).]

$\bar{C}$ on saponification with standard alk. (Sap. Eq. = 108 5), followed by acidification, yields 3,6-dichlorophthalic acid (3:4870) q.v.

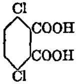
3:4860 (1) Pratt, Perkins, *J. Am. Chem. Soc.* **40**, 214–218 (1918). (2) Graebe, *Ber.* **33**, 2019–2022 (1900). (3) Villiger, *Ber.* **42**, 3538–3541, 3549 (1909). (4) Faust, *Ann.* **160**, 64 (1871). (5) Pfeiffer, *Ber.* **55**, 425 (1922). (6) Widman, *Bull. soc. chim.* (2) **28**, 512 (1877). (7) Krescheck, Ullmann, *Ber.* **55**, 308 (1922). (8) Le Royer, *Ann.* **238**, 350–361 (1887). (9) Harrop, Norris, Weizmann, *J. Chem. Soc.* **95**, 282–283 (1909). (10) Tingle, Bates, *J. Am. Chem. Soc.* **32**, 1323–1325 (1910).

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* **1936**, I 2830; *C.A.* **30**, 1394 (1936). (12) Mueller (to General Aniline Works, Inc.), U.S. 1,997,226, April 6, 1935; *Cent.* **1935**, II 1449. (13) Hodgson, *J. Soc. Dyers Colourists* **49**, 215 (1933). (14) Imperial Chem. Ind., Ltd., French 749,954, Aug. 2, 1933; *Cent.* **1933**, II 2748–2749. (15) Kirpal, Galuschka, Lassak, *Ber.* **68**, 1332–1333 (1935). (16) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934; *Cent.* **1934**, II 3047. (17) Ullmann, Billig, *Ann.* **381**, 14–16 (1911). (18) Dougherty, Gleason, *J. Am. Chem. Soc.* **52**, 1027 (1930). (19) Walsh, Weizmann, *J. Chem. Soc.* **97**, 687, 691 (1910) (20) Egerer, Meyer, *Monatsh.* **34**, 90 (1913).

(21) Eckert, Endler, *J. prakt. Chem.* (2) **102**, 334 (1921). (22) Jaroschy, *Monatsh.* **34**, 2 (1934). (23) Keimatsu, Hirano, *J. Pharm. Soc. Japan* **49**, 20–26 (1929), **50**, 61–63 (1930); *Cent.* **1929**, I 2533, **1930**, II 1551. (24) Keimatsu, Hirano, Yoshimi, *J. Pharm. Soc. Japan* **50**, 95–98 (1930); *Cent.* **1930**, II 2384. (25) Barnett, Goodway, Watson, *Ber.* **66**, 1890 (1933). (26) I.G., French 642,662, Sept. 1, 1928; *Cent.* **1929**, I 581. (27) Kramer (to I.G.), Ger. 589,145, Dec. 2, 1933; *Cent.* **1934**, I 771. (28) Kränzlein, Greune, Sedlmayr (to I.G.), Ger. 430,558, Aug. 13, 1926; *Cent.* **1926**, II 2230. (29) Frey, *Ber.* **45**, 1359 (1912). (30) Waldmann, *J. prakt. Chem.* (2) **126**, 251–253 (1930).

(31) Mariott, Robinson, *J. Chem. Soc.* **1934**, 1633. (32) Pratt, Perkins, *J. Am. Chem. Soc.* **40**, 234 (1918). (33) Juvalta, Ger. 50,117, *Friedländer* II-93. (34) Lesser, Weiss, *Ber.* **46**, 3945 (1913). (35) Durand, Hueguenin, S.A. Brit. 251,644, July 7, 1926; *Cent.* **1927**, I 1228. (36) Imperial Chem. Ind., Ltd., French 808,845, Feb. 16, 1937; *Cent.* **1937**, II 3820. (37) Imperial Chem. Ind., Ltd , Thorpe, Linstead, Brit. 390,119, April 27, 1933; French 737,392, Dec. 10, 1932; *Cent.* **1933**, II 794. (38) Dreyfus, French 749,792, July 29, 1933; *Cent.* **1934**, I 3154. (39) Graebe, Gourevitz, *Ber.* **33**, 2024–2025 (1900). (40) Drew, Pearman, *J. Chem. Soc.* **1937**, 31–32.

(41) Mariott, Robinson, *J. Chem. Soc.* **1939**, 137–138.

3:4870 3,6-DICHLOROPHTHALIC ACID  $C_8H_4O_4Cl_2$ **Beil. IX-817** **IX_1—**

M.P. See text.

[*See also 3,6-dichlorophthalic anhydride* (3:4860).]

Tbls. from aq.; eas. sol. hot aq. in which it readily gives supersatd. solns.; eas. sol. alc., ether.

$\bar{C}$ on htg. begins to lose aq. even at 100° with formn. of 3,6-dichlorophthalic anhydride (3:4860) cf. (1); this change proceeds with increasing speed as the temperature increases; for this reason no definite m.p. of $\bar{C}$ is recorded and the m.p. observed is actually that of the anhydride.

[For prepn. of $\bar{C}$ from 3,6-dichlorophthalic anhydride by hydrolysis see the anhydride

(3:4860); from ethyl hydrogen 3,6-dichlorophthalate by htg. at 200° to convert to the anhydride and hydrolysis of the latter see (1); from 1,4-dichloronaphthalene (3:1655) by boilg. with HNO_3 (D = 1.3) see (2); from 1,4,5-trichloronaphthalene (3:4005) by htg. with HNO_3 in s.t. see (3); from "α-tetrachloronaphthalene" [Beil. V-546] by oxidn with HNO_3 see (4); from 1,4-dichloronaphthalene tetrachloride (1,2,3,4,5,8-hexachlorotetralin) [Beil. V-493] by boilg. with conc. HNO_3 (D = 1.42) see (5) (6); from 5,8-dichloronaphthylamine-2 [Beil. XII-1310] on oxidn. with dil. HNO_3 in s t. at 180–200° see (7).]

[For sepn of $\bar{C}$ from mixts. with the isomeric 3,4- (3:4880) and 4,5- (3:4890) dichlorophthalic acids see (8) (9).] [For use of $\bar{C}$ as softener and/or plasticizer for cellulose derivs. see (10).]

Salts. $NH_4H\bar{A}$, $NaH\bar{A}$, $KH\bar{A}$, as well as $(NH_4)_2\bar{A}$, $Na_2\bar{A}$, and $K_2\bar{A}$, are all eas. sol. aq. (8); $Ag_2\bar{A}$, insol. aq. (8) (12); $Ca\bar{A}$, $4H_2O$ (5) (12), spar. sol. aq. and pptd. by $CaCl_2$ from hot dil. aq. solns. of $(NH_4)_2\bar{A}$ (8) (12); $Ba\bar{A}$, H_2O, spar. sol. aq. (5) (12); $Zn\bar{A}$, eas. sol. aq. (characteristic dif. from 3,4- and 4,5-dichlorophthalic acids and used in sepn. of $\bar{C}$ (8)).

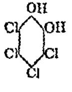
Esters. Dimethyl 3,6-dichlorophthalate, m p 82° (11) (from $Ag_2\bar{A}$ with MeI (11)); methyl hydrogen 3,6-dichlorophthalate, unreported; diethyl 3,6-dichlorophthalate, cryst. from 50% alc., m p 60° (12) (13) (from $Ag_2\bar{A}$ on htg. with EtI in s.t. at 100° (12) (13), or in very small yield from ethyl hydrogen 3,6-dichlorophthalate with EtOH (1) (14)); ethyl hydrogen 3,6-dichlorophthalate, cryst. from CCl_4, m p. 130–131° (8), 128–130° (1), 128–129° (15) (from 3,6-dichlorophthalic anhydride (3:4860) with EtOH).

[For studies of ionization consts. of first (16) and second (16) (17) acid groups see indic. refs.]

3:4870 (1) Graebe, *Ber.* **33**, 2020–2023 (1900). (2) Atterberg, *Bull soc. chim.* (2) **27**, 409 (1877); *Ber.* **10**, 547 (1877). (3) Atterberg, *Bull soc. chim.* (2) **27**, 407 (1877); *Ber.* **9**, 1734–1735 (1876). (4) Widman, *Bull soc. chim.* (2) **28**, 511–512 (1877). (5) Faust, *Ann.* **160**, 64–65 (1871). (6) Widman, *Ber.* **15**, 2160 (1882). (7) Claus, Philipson, *J. prakt. Chem.* (2) **43**, 61 (1891). (8) Villiger, *Ber* **42**, 3538–3539 (1909). (9) Hodgson, *J. Soc Dyers Colourists* **49**, 215 (1933). (10) Dreyfus, French 749,792, July 29, 1933, *Cent* **1934**, I 3154.

(11) Kirpal, Galuschka, Lassak, *Ber.* **68**, 1332–1334 (1935) (12) Le Royer, *Ann.* **238**, 351–354 (1887) (13) Graebe, Gourevitz, *Ber.* **33**, 2024 (1900). (14) Graebe, Rostowzew, *Ber.* **34**, 2108–2109 (1901) (15) Pfeiffer, *Ber.* **55**, 425 (1922) (16) Wegscheider, *Monatsh.* **23**, 325–326 (1902). (17) Berger, *Helv. Chim. Acta* **23**, 41–44, 50–52 (1940).

3:4875 TETRACHLOROPYROCATECHOL (Tetrachlorocatechol, tetrachloro-1,2-dihydroxybenzene)



$C_6H_2O_2Cl_4$ Beil. VI - 784; VI_1-(389); VI_2-(787)

M.P. 194–195° (1)
194° (2)
193–194° (3)

[*See also tetrachlorobenzoquinone*-1,2 (3:3965).]

Colorless anhydrous cryst from hot dil. alc (1), lgr. (1) or C_6H_6 (2); $\bar{C}$ from dil. AcOH seps. as monohydrate which over $CaCl_2$ loses half of its water and above 70–80° all of its aq (3) (4); $\bar{C}$ from AcOH seps. as a cpd., $\bar{C}$.AcOH, m.p. 123–124° (4), which can be recrystd. unchanged from lgr. but in air or more rapidly over alk. loses its cryst. AcOH; the above cpd. on soln in alc and pptn. with much aq. yields a trihydrate, $\bar{C}.3H_2O$, m p. 94°, which can be recrystd unchanged from aq , alc., or acetone but which from C_6H_6 or lgr seps. $\bar{C}$ in anhydrous form (4)

[For prepn. of $\bar{C}$ from pyrocatechol (1:1520) with Cl_2 in AcOH (5) (2) (13) or with ICl

(3) see indic. refs.; from hexachlorocyclohexene-3-dione-1,2 [Beil. VII-575] by reductn. with $SnCl_2$ in AcOH see (1).]

$\bar{C}$ with std. alk. (using phenolphthalein) titrates sharply as a monohydric phenol (4) (6), i.e., Neut. Eq. 248; similarly titration of the cpd. $\bar{C}$.AcOH (above) gives Neut. Eq. 154 (4).

$\bar{C}$ on oxidn. with fumg. HNO_3 in AcOH gives (81% yield (13)) (1) (5) (7) (8) tetrachloro-*o*-benzoquinone-1,2 (3:3965). — For study of oxidn.-reductn. potential of system: $\bar{C}$ + tetrachlorobenzoquinone-1,2 see (7) (8). — $\bar{C}$ with equiv. tetrachlorobenzoquinone-1,2 (3:3965) in least possible hot $CHCl_3$ gives on cooling the corresp. quinhydrone (14). — [For other complex prods. obtd. from $\bar{C}$ by action of conc. HNO_3 or N_2O_4 (9), HNO_3 + H_2SO_4 (10), or $NaNO_2$ in AcOH (2) see indic. refs.]

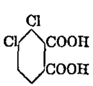
Ⓓ Tetrachloropyrocatechol diacetate: ndls. from AcOH, m.p. 190° (1). [From $\bar{C}$ with Ac_2O (1).]

—— Tetrachloropyrocatechol monomethyl ether (tetrachloroguaiacol) [Beil. VI-784]: ndls. from hot aq., m.p. 185–186° (11). [Reported only by indirect means (11).]

—— Tetrachloropyrocatechol dimethyl ether (tetrachloroveratrole) [Beil. VI-784]: ndls. from alc., m.p. 88° (11) (12). [Reported only by indirect means (11) (12).]

3:4875 (1) Zincke, Küster, *Ber.* **21**, 2729–2730 (1888). (2) Frejka, Sefranek, Zika, *Collection Czechoslov. Chem. Commun.* **9**, 241–242 (1937); *Cent.* **1937**, II 1816; *C.A.* **31**, 7046–7047 (1937). (3) Jackson, Boswell, *Am. Chem. J.* **35**, 528–531 (1906). (4) Willstatter, Müller, *Ber.* **44**, 2186 (1911). (5) Zincke, *Ber.* **20**, 1779 (1887). (6) Weissberger, *Ber.* **65**, 1820 (1932). (7) Conant, Fieser, *J. Am. Chem. Soc* **46**, 1873, 1875 (1924). (8) Kvalnes, *J. Am. Chem. Soc.* **56**, 2487–2489 (1934). (9) Zincke, *Ann.* **435**, 161–162 (1924). (10) Zincke, Weishaupt, *Ann.* **437**, 93–94 (1924).

(11) Brüggemann, *J. prakt. Chem.* (2) **53**, 251 (1896). (12) Cousin, *Ann. chim.* (7) **29**, 87 (1903). (13) Jackson, MacLaurin, *Am. Chem. J.* **37**, 11 (1907). (14) Jackson, Carleton, *Am. Chem. J.* **39**, 497 (1908).

3:4880 3,4-DICHLOROPHTHALIC ACID  $C_8H_4O_4Cl_2$ Beil. IX-817 IX_1—

M.P. abt. 195° rap. htg. (1)

[*See also* 3,4-*dichlorophthalic anhydride* (3:3695).]

Rectangular tbls. from aq.; eas sol. aq , ether — $\bar{C}$ can only with difficulty be separated from 4,5-dichlorophthalic acid (3:4890) by crystn. (1).

[For prepn. from 3,4-dichlorophthalic anhydride (3:3695) on boilg. with aq. see (1); from *N*-(hydroxy)-3,4-dichlorophthalimide (see under 3,4-dichlorophthalic anhydride) by hydrolysis with hot 10% HCl see (1).]

[For sepn. of $\bar{C}$ from mixts. with the isomeric 3,6- (3:4870) and 4,5- (3:4890) dichlorophthalic acids see (1) (2).]

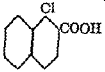
Salts. $NaH\bar{A}$, $Ag_2\bar{A}$, $Cu\bar{A}$, $Ca\bar{A}$, $Ba\bar{A}$, $Zn\bar{A}$ all spar. sol. aq. (1).

Esters. Methyl hydrogen 3,4-dichlorophthalate and dimethyl 3,4-dichlorophthalate *are both unreported: both possible ethyl hydrogen 3,4-dichlorophthalates* are known, viz., ethyl 2-carboxy-3,4-dichlorophthalate (from $\bar{C}$ + abs. EtOH + few drops conc. H_2SO_4 refluxed 6 hrs. (3)), ndls. from dil. alc., m p. 184° (3); and 3,4-dichloro-2-carbethoxybenzoic acid (from diethyl 3,4-dichlorophthalate by partial KOH saponification or from the anhydride with abs. EtOH (3)), pr. from dil. alc , m p. 164° (3): diethyl 3,4-dichlorophthalate (from $Ag_2\bar{A}$), m.p. 80° (3). [For the *pseudo* diethyl ester of $\bar{C}$ see under 3,4-dichlorophthalic anhydride (3:3695).]

$\bar{C}$ on protracted htg. at 220° loses aq yielding 3,4-dichlorophthalic anhydride (3:3695) q.v.

3:4880 (1) Villiger, *Ber.* 42, 3538–3539, 3541–3542 (1909). (2) Hodgson, *J. Soc Dyers Colourists* 49, 215 (1933). (3) Kirpal, Galuschka, Lassak, *Ber.* 68, 1333–1334 (1935).

3:4885 1-CHLORONAPHTHOIC ACID-2 $C_{11}H_7O_2Cl$ Beil. IX - 661
IX_1—



M.P. 196° (1) (2)
195° (3)

Ndls. from C_6H_6 (1) (2) or from 50% AcOH (3). — Volatile without decompn. (1).

[For prepn of $\bar{C}$ from 2-(1-chloronaphthyl)carbinol (2) by oxidn. see (2); from 1-chloro-2-(trichloromethyl)naphthalene [Beil. V-568] by hydrolysis in boilg AcOH contg a little aq see (1), from 1-chloro-2-naphthonitrile (see below) by hydrolysis with $AcOH/H_2SO_4$/aq. mixt. see (4), from methyl 1-chloro-2-naphthoate (see below) by hydrolysis with boilg. *15% alc KOH (46% yield) see (3).*]

$\bar{C}$ with 2% Na/Hg in aq. reduces (1) to β-naphthoic acid (1:0800), m p 184° (1).

[The direct conv. of $\bar{C}$ to 1-chloro-2-naphthoyl chloride is not actually reported; however, this acid chloride, m p 59–60 5° (6), b p 226° at 150 mm. (6), b.p. 199–200° at 11.2 mm (5), has been obtained (5) (3) (6) from 1-hydroxy-2-naphthoic acid [Beil. X-331, X_1-(145)] with PCl_5 (*yield 60 7% (5)*) (2).]

Salts. $Ag\bar{A}$, white flocks spar sol aq., $Ca\bar{A}_2.2H_2O$, cryst from aq. (1).

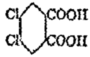
—— Methyl 1-chloro-2-naphthoate: ndls. from alc, m.p. 50° (2), cryst from pet. eth. + acetone, m p 44–48° (5), b.p 189–193° at 17 5 mm (3), 186 5–189° (but press. not given) (5). [From $\bar{C}$ in MeOH with HCl gas (2) *or from the acid chloride (above)* in boilg MeOH (5) (3).] [This ester with Cu bronze + a trace of I_2 at 290° yields (5) dimethyl 1,1′-binaphthyl-2,2′-dicarboxylate.]

—— Ethyl 1-chloro-2-naphthoate: unreported.

—— 1-Chloro-2-naphthonitrile: colorless ndls. from MeOH but m.p not stated (4), *b.p. 183–184° at 11 mm (4). [From 1-chloro-2-naphthylamine [Beil XII-1308,* XII_1-(542)] by diazotization and reactn. with $KCu(CN)_2$ (4).]

3:4885 (1) Wolffenstein, *Ber.* 21, 1190–1191 (1888). (2) Achmatowicz, Lindenfeld, *Roczniki Chem.* 18, 69–74 (1938); *Cent* 1939, II 389, not in *C.A* (3) Bergmann, Hirshberg, *J. Chem. Soc.* 1936, 333. (4) Willstaedt, Scheiber, *Ber* 67, 473–474 (1934). (5) Kuhn, Albrecht, *Ann* 465, 283–285 (1928) (6) *Strohbach, Ber. 34, 4161 (1901).*

3:4890 4,5-DICHLOROPHTHALIC ACID $C_8H_4O_4Cl_2$ Beil. IX - 818
IX_1-(366)



M.P. 199–200° (1)
200° rap htg. (2)

[*See also 4,5-dichlorophthalic anhydride* (3:4830).]

Ndls. from aq.

[For prepn. of $\bar{C}$ from 4,5-dichlorophthalic anhydride (3:4830) by hydrolysis see (2)

(3); from aq. soln. of alk. salts of phthalic acid (1:0820) with Cl_2 in pres. of Sb cpds. see (3) (4); from 4,5-dichloro-1,2-dimethylbenzene (1) by oxidn. with dil. HNO_3 ($D = 1.3$) in s.t. at 180° for 7 hrs. see (1) cf. (5) (6).]

[For sepn. of $\bar{C}$ from mixts. with the isomeric 3,4- (3:4880) and 3,6- (3:4870) dichlorophthalic acids see (2) (8).] — [For use of $\bar{C}$ as softener for cellulose derivs. see (9).]

Salts. $NH_4H\bar{A}$, $NaH\bar{A}$, $KH\bar{A}$ (all from aq. solns. of the corresp. eas. sol. neutral salts by addn. of AcOH) are spar. sol. cold aq. (2): $Cu\bar{A}$, $Ca\bar{A}$, $Ba\bar{A}$, $Zn\bar{A}$, and $Ag_2\bar{A}$ are all spar. sol. (2).

Esters. Dimethyl 4,5-dichlorophthalate and diethyl 4,5-dichlorophthalate are unreported; methyl hydrogen 4,5-dichlorophthalate is unreported, but ethyl hydrogen 4,5-dichlorophthalate, ndls. from $CHCl_3$, m.p. 133–134°, is obtained from the anhydride (3:4830) with EtOH (2).

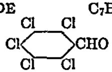
[$\bar{C}$ on fusion with NaOH at 175–185° gives (small yield (3)) 4,5-dihydroxyphthalic acid [Beil. X-552, X_1-(276)], m.p. 175°.

$\bar{C}$ on htg. loses H_2O yielding (2) 4,5-dichlorophthalic anhydride (3:4830), m.p. 187°.

Ⓓ Di-(*p*-nitrobenzyl) 4,5-dichlorophthalate: cryst. from alc., m.p. 164.5° (10). [From $Na_2\bar{A}$ with *p*-nitrobenzyl bromide (2 moles) htd. in alc. (10).]

3:4890 (1) Hinkel, Ayling, Bevan, *J. Chem. Soc.* **1928**, 1876. (2) Villiger, *Ber.* **42**, 3538–3539, 3546–3547 (1909). (3) Rushchinskii, *J. Applied Chem.* (*U.S.S.R.*) **7**, 1113–1115 (1934); *Cent.* **1936**, II 2902. (4) Rushchinskii, Russ. 41,515, Feb. 28, 1935; *Cent.* **1935**, II 3704; *C.A.* **30**, II 2902. (5) Claus, Kautz, *Ber.* **18**, 1369–1370 (1885). (6) Claus, Groneweg, *J. prakt. Chem.* (2) **43**, 253–254 (1891) (7) Ref. 2, pp. 3532–3533. (8) Hodgson, *J. Soc. Dyers Colourists* **49**, 215 (1933). (9) Dreyfus, French 749,792, July 29, 1933; *Cent.* **1934**, I 3154. (10) Lyons, Reid, *J. Am. Chem. Soc.* **39**, 1741, 1744 (1917).

3:4892 PENTACHLOROBENZALDEHYDE C_7HOCl_5 Beil. VII — VII_1-(134)



M.P. 202.5° (1) (2)
197–199° (3)

Colorless ndls. from C_6H_6/alc.; eas. sol. hot C_6H_6 or CS_2; spar. sol. alc., ether, lgr.

[For prepn. of $\bar{C}$ from pentachlorobenzal (di)chloride (3:3590) by hydrolysis with conc. H_2SO_4 at 60–100° or fumg. H_2SO_4 at 40–50° (90% yield (2)) (3) see indic. refs.; from pentachlorobenzaldehyde diethylacetal (see below) by acid hydrolysis see (1).]

$\bar{C}$ with aq. alk. $KMnO_4$ refluxed 7 hrs. oxidizes to (90% yield (1)) pentachlorobenzoic acid (3:4910).

$\bar{C}$ in C_6H_6 shaken with satd. aq. $NaHSO_3$ soln. gives (1) the corresp. $NaHSO_3$ cpd.

$\bar{C}$ with aq. 50% KOH at 100° for 5 hrs. suffers hydrolytic cleavage giving (88% yield (2)) pentachlorobenzene (3:2290) and potassium formate.

$\bar{C}$ with EtOH + dry HCl gas gives (60% yield (1)) pentachlorobenzaldehyde diethylacetal, colorless cryst. from pet. ether, m.p. 45°.

[For use of $\bar{C}$ on prepn. of dyes of the triphenylmethane series see (4).]

$\bar{C}$ reacts normally with RMgX reagents [e.g., $\bar{C}$ with MeMgBr gives (49% yield (1)) methyl-pentachlorophenyl-carbinol, colorless cryst. from alc., m.p. 126° (1); $\bar{C}$ with C_6H_5-MgBr gives (1) phenyl-pentachlorophenyl-carbinol (pentachlorobenzohydrol), cryst. from C_6H_6, m.p. 117°.]

$\bar{C}$ with anhydrous NaOAc + Ac_2O (Perkin synthesis) at 170–180° for 60 hrs. gives (30% yield (1)) 2,3,4,5,6-pentachlorocinnamic acid, cryst. from C_6H_6, m.p. 233° cor. (1).

C̃ with aniline at 100° condenses giving (1) pentachlorobenzaldehyde anil, greenish ndls. from C_6H_6/alc., m.p. 187.5° cor. (1).

Ⓓ Pentachlorobenzaldoxime: colorless ndls. from C_6H_6, m.p. 201° cor. (1). [From C̃ with $NH_2OH \cdot HCl$ + Na_2CO_3 in dil alc. on stdg. few days (1).]

Ⓓ Pentachlorobenzaldehyde phenylhydrazone: citron-yel. ndls. from alc., m.p. 152.5° cor. (1) [From C̃ in hot satd C_6H_6 soln with 1 mole phenylhydrazine (1).]

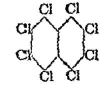
—— Pentachlorobenzaldehyde *p*-nitrophenylhydrazone: unreported.

—— Pentachlorobenzaldehyde 2,4-dinitrophenylhydrazone: unreported.

—— Pentachlorobenzaldehyde semicarbazone: unreported.

3:4892 (1) Lock, *Ber* 72, 300–304 (1939). (2) Lock, *Ber* 66, 1533 (1933). (3) Bayer and Co., Ger 243,416, Feb. 10, 1912, *Cent* 1912, I 618; [*C.A.* 6, 2292 (1912)] U.S. 998,140, July 18, 1911; [*C.A.* 5, 2904–2905 (1911)] (4) Bayer and Co., Ger. 234,519, May 12, 1911; *Cent.* 1911 I 1620; [*C.A* 5, 2974 (1911)]

3:4893 OCTACHLORONAPHTHALENE (Perchloronaphthalene)



$C_{10}Cl_8$ Beil. V - 547, V_1—, V_2-(446)

M.P.		B.P.	
203° (1) u.c.	(8)	440–442° at 754 mm., dec.	(2)
202° u.c.	(7)	258–260° at 2.5 mm.	(2)
200°	(6)	246–250° at 0.5 mm.	(2)
197.5–198° cor.	(2)		
197.3–198° cor.	(3)		

Ndls. from CCl_4 + C_6H_6 (2); fairly eas. sol. C_6H_6, lgr., $CHCl_3$; spar. sol. alc. or AcOH.

[For prepn. of C̃ from naphthalene (1:7200) with Cl_2 in pres. of 1% Fe powder + 0.1% I_2 first at 100° then at 150° for 10–12 hrs (90% yield (2)) or with Cl_2 in pres. of $SbCl_5$ (1) (4) cf (2) see indic refs. (for extensive study of merits of many catalysts see (5)).]

[For prepn. of C̃ from mixt. of 2-hydroxynaphthalene-1,5-*bis*-(sulfonyl chloride) and 2-hydroxynaphthalene-1,6-*bis*-(sulfonyl chloride) (from β-naphthol with $ClSO_3H$) with PCl_5 in s.t. see (6), from 1-hydroxynaphthalene-*tris*-(sulfonyl chloride) with PCl_5 in s.t. at 250° see (7); from 1-amino-3,6,8-*tris*-(sulfonyl chloride) with 3–4 pts. PCl_5 in s.t. at 200–225° for 7 hrs. (40% yield) see (2).]

[For prepn. of C̃ from 2,5,6,7,8-pentachloronaphthoquinone-1,4 (Beil. VII-731) with PCl_5 in s.t. at 250° for 6 hrs. see (8); from hexachloronaphthoquinone-1,4 (see below) with PCl_5 see (3).]

[For study of action of C̃ (from insulation material on electric wiring) in production of acne see (9); for prepn. of aq. dispersions of C̃ see (10); for use of C̃ as insecticide see (11); for use of C̃ in prepn. of a red mordant dyestuff (by actn. of fumg. H_2SO_4) see (12).]

[C̃ with H_2 passed through a red-hot tube (4) or C̃ with Na + EtOH (2) gives naphthalene (1:7200) together with other prods.]

C̃ on oxidn. with 10 pts. fumg. HNO_3 (D = 1.52) in s.t. at 90° gives in good yield (2) (3) hexachloronaphthoquinone-1,4, m.p. 222.5° cor., b.p. 412–415° at 758 mm. dec., 265–267° at 14 mm., accompanied by some tetrachlorophthalic acid (3:4946).

[C̃ on htg. with $SbCl_5$ + ICl in s.t. at 350° (1) breaks down yielding (2) cf. (1) carbon tetrachloride (3:5100), hexachloroethane (3:4835), hexachlorobenzene (3:4939), and other prods.; under certain conditions (not specified in abstracts) C̃ can be broken down to decachloroindane (perchlorohydrindene) [Beil. V-487], m.p. 138° cor. (2).]

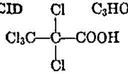
[$\bar{C}$ with pyridine + CuO + hydrazine hydrate yields (13) a hexachloronaphthalene ndls. from chlorobenzene, m p. 202–204° (13) (note that m.p. is close to that of $\bar{C}$).]

$\bar{C}$ is stable toward 3% aq. KOH or NaOH for 12 hrs. in cold or even 2 hrs. boilg.; $\bar{C}$ is stable to cold 3% alc. KOH or NaOH for 24 hrs., but on htg. for 2 hrs. splits off some 25–30% chlorine and in part resinifies (2).

Ⓟ *Color test with $SbCl_5$ in CCl_4: $\bar{C}$ with $SbCl_5$ in CCl_4 gives stable cherry-red color* (2). [This response is not given by carbon tetrachloride (3:5100), hexachloroethane (3:4835), hexachlorobenzene (3:4939), or decachloroindane (2).]

3:4893 (1) Ruoff, *Ber.* **9**, 1486–1488 (1876). (2) Shvemberg, Gordon, *J. Gen Chem* (*U.S.S.R.*) **2**, 921–928 (1932); *Cent* **1934**, I 215; *C.A.* **27**, 2139 (1933). (3) Shvemberg, Gordon, *J. Gen. Chem.* (*U S.S.R*) **4**, 695–703 (1934); *Cent.* **1935**, II 514; *C.A.* **29**, 2162 (1935). (4) Berthelot, Jungfleisch, *Bull. soc. chim* (2) **9**, 446–455 (1868); *Ann chim.* (4) **15**, 330–343 (1868). (5) Shvemberg, Gordon, *J Gen. Chem* (*U.S.S.R.*) **4**, 529–551 (1934); *Cent.* **1935**, II 514; *C.A.* **29**, 1804 (1935) (6) Pollak, Gebauer-Fulnegg, Blumenstock-Halward, *Monatsh.* **49**, 199 (1928). (7) Claus, Mielcke, *Ber.* **19**, 1186–1187 (1886). (8) Claus, Wenzlik, *Ber.* **19**, 1169 (1886). (9) Haldin-Davis, *Brit. J. Dermatol. Syphilis* **51**, 380–383 (1939), *C.A.* **34**, 1413 (1940). (10) Heckert (to du Pont Rayon Co.), U.S. 2,060,210, Nov. 10, 1936; *Cent.* **1937**, I 1604; *C.A.* **31**, 555 (1937).
(11) Stern, Ger. 411,314, March 26, 1925; *Cent.* **1925**, II 234. (12) B.A S.F., Ger. 66,611, *Friedländer* **3**, 271. (13) I.G., French 699,492, Feb. 16, 1931; *Cent.* **1931**, 3519.

3:4895 PENTACHLOROPROPIONIC ACID



$C_3HO_2Cl_5$ Beil. II — II_1-(112) II_2-(228)

M.P. 200–215° (see text (1)).

Colorless cryst. from CCl_4. — Eas sol cold aq.

[For prepn. of $\bar{C}$ from trichloroacrylic acid (3:1840) with Cl_2 in CCl_4 soln. in sunlight (yield not reported) see (1)]

$\bar{C}$ in aq. soln. behaves as a strong acid; on titration it gives a good Neut. Eq., calcd. 246.5; found 245.8 (1).

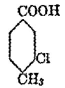
$\bar{C}$ is very unstable: e.g., $\bar{C}$ in aq. soln. on warming dec. (1) (with loss of HCl and CO_2) into tetrachloroethylene (3:5460); presumably this same decompn. occurs on process of taking its m.p., and the value given above refers to rapid htg. on Hg bath.

Salts. The salts of $\bar{C}$ can be obtd. by neutralization with metal hydroxide of a cold satd. aq soln. of $\bar{C}$ followed by evapn. to dryness at low temp.; aq. solns. of the salts are also unstable and rapidly decompose yielding metal chloride + CO_2 + tetrachloroethylene (3:5460) (1). [For studies of influence of light on decompn. of these salts see (2) (3) cf. (4).]

[For study of behavior of $\bar{C}$ with H_2 + colloidal Pd see (5).]

Acid chloride. Pentachloropropionyl chloride (3:0470) has been obtd. indirectly, i.e , from trichloroacryloyl chloride with Cl_2 in sunlight (6); colorless cryst., m.p 42°.

3:4895 (1) Boeseken, *Rec. trav. chim.* **46**, 841–843 (1927). (2) Jaeger, *J. Chem. Soc.* **119**, 2070–2076 (1921). (3) Jaeger, Berger, *Rec. trav. chim.* **41**, 72 (1921). (4) Jaeger, *Cent.* **1912**, I 1817–1818; *Cent.* **1911**, II 1851. (5) Boeseken, *Rec. trav. chim.* **35**, 273–274 (1915). (6) Boeseken, Hasselbach, *Rec. trav. chim.* **32**, 11–14 (1913).

3:4900 3-CHLORO-4-METHYLBENZOIC ACID  $C_8H_7O_2Cl$ Beil. IX - 498 IX_1—

M.P. 200–202° (1)
199–201° cor. (2)
199° (3)
196° (4) (5)
195–197° (6)
194–196° u.c. (2)
194–195° (7)

Long colorless ndls. from dil. alc.; spar. sol. hot aq ; eas. sol. cold alc.

[For prepn. of C̄ from 2-chloro-4-isopropyl-methylbenzene (2-chloro-p-cymene) (3:8775) by oxidn. with dil. HNO_3 (7) of D = 1 24 for 8–14 days (2) or htd. 6 hrs. with 5 pts. HNO_3 (D = 1.39) + 5 pts. aq. (4) see indic. refs ; from 3-chloro-1,4-dimethylbenzene (2-chloro-p-xylene) (3.8600) by oxidn with nitrosulfonic acid + fumg. HNO_3 see (1) (5); from 3-chloro-4-methylacetophenone (8) by oxidn. with alk. $KMnO_4$ see (8); from 3-chloro-4-methylbenzaldehyde (5) with 50% KOH (Cannizzaro reactn.) see (5); from 3-chloro-4-methylbenzonitrile, m.p. 48–48.5° u c. (3), 45–46° (6), by protracted boilg with aq. KOH see (3), from 3-chloro-4-methylbenzamide (see below) on hydrolysis with 25% aq. NaOH see (6).]

Salts. *KĀ.1½H₂O*, eas sol. aq. (9); $Ca\bar{A}_2.3H_2O$, $Ba\bar{A}_2.4H_2O$ (7).

C̄ on fusion with KOH yields (7) (2) 3-hydroxy-4-methylbenzoic acid [Beil. X-237].

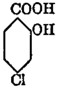
[C̄ on mononitration (9) yields a mixt. of three mononitro derivs containing 60–70% *3-chloro-4-methyl-6-nitrobenzoic acid* [Beil IX-503], *ndls. from alc., m.p. 184–185°* (9), 20–30% 3-chloro-4-methyl-5-nitrobenzoic acid [Beil. IX-503], ndls. from aq., m.p. 159° u c. (9), and 5–10% 3-chloro-4-methyl-2-nitrobenzoic acid [Beil IX-503], lfts from aq., m.p. 211° (9).]

—— **Ethyl 3-chloro-4-methylbenzoate:** oil, b p. 129–130° at 9 mm., $D_4^{19.2}$ = 1.1658, $n_{He}^{19.2}$ = 1.52531 (10). [Note that for the b.p. 149–150° formerly reported (3) no pressure is given.]

—— **3-Chloro-4-methylbenzamide:** lfts. from aq., alc., or aq. alc., m p. 173–175° (6). [From partial hydrolysis of 3-chloro-4-methylbenzonitrile (above) with aq. alk. (3) (6), further hydrolysis yields (6) C̄.]

3:4900 (1) Varma, Ramon, *J. Indian Chem. Soc* **12**, 541 (1935). (2) Vongerichten, *Ber.* **11**, 365–368 (1878) (3) Claus, Davidsen, *J. prakt Chem.* (2) **39**, 497–498 (1889). (4) Hintikka, *Ann. Acad Sci Fennicae* **19-A**, No. 10, 6 pp. (1923), *C.A* **19**, 42 (1925). (5) Wahl, *Compt. rend.* **198**, 1613–1614 (1934). (6) Magidson, Trawin, *Ber* **69**, 538–539 (1936). (7) Vongerichten, *Ber.* **10**, 1249–1250 (1877). (8) Ganguly, LeFevre, *J. Chem Soc.* **1934**, 852. (9) Claus, Böcher, *Ann.* **265**, 356–363 (1891). (10) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 17–18 (1929).

3:4908 4-CHLORO-2-HYDROXYBENZOIC ACID $C_7H_5O_3Cl$ Beil. X - 101
(4-Chlorosalicylic acid) X_1-(47)



M.P. [211° (1)]
207.5° (2)
207° (3) (4)
206–207° (5)

Colorless ndls. from aq.; spar. sol. aq., eas. sol. alc., C_6H_6, $CHCl_3$. — Volatile with steam; sublimes with slight decompn.

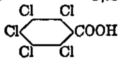
[For prepn. of C̄ from *m*-chlorophenol (3:0255) by treatment of dry sodium salt with CO_2 at 140–150° under press. see (3); from 4-chloro-2-aminobenzoic acid (4-chloroanthranilic acid) [Beil. XIV-365, XIV_1-(548)] via diazotization and boilg. with aq. see (3) (5); from 7-chloro-2,3-dimethylchromone [Beil. $XVII_1$-(177)] on boilg. with 4% aq. NaOH see (2); for formn. of C̄ from *p*-chlorobenzoic acid (3:4940) by electrolytic oxidn. in acid soln. see (4); from 4-chloro-2-methoxybenzoic acid (see below) by cleavage with HI see (1).]

C̄ in aq. soln. gives with $FeCl_3$ a purple color.

[The methyl ether of C̄, viz., 4-chloro-2-methoxybenzoic acid, cryst. from aq., m.p. 148° (1), has been obtd. from 4-chloro-2-methoxybenzaldehyde (1) by oxidn. with aq. alk. $KMnO_4$ (1).]

3:4908 (1) Hodgson, Jenkinson, *J Chem. Soc.* **1927**, 1741–1742. (2) Simonis, Schuhmann, *Ber.* **50**, 1146–1147 (1917). (3) Varnholt, *J. prakt. Chem.* (2) **36**, 27–31 (1887). (4) Fichter, Adler, *Helv. Chim. Acta* **9**, 283 (1926). (5) Cohn, *Mitt. Technol. Gewerb.-Mus. Wien*, **11**, 178–182; *Cent.* **1901**, I 925.

3:4910 PENTACHLOROBENZOIC ACID $C_7HO_2Cl_5$ Beil. IX - 347
IX_1-(142)



M.P. 208° cor. (1)
201° (2)
200° (3)
199–200° u.c. (4)
199.5° (5)

Ndls. or pr.; sublimes in vac. with slight decomposition (6). Very sol. toluene or alc. (5). — Best recrystd. from toluene + lt. pet. ether (5). — Can be recrystd. from C_6H_6 or dil. AcOH (6). — From alc. C̄ (despite its high m.p.) first separates as an oil (5).

[For prepn. of C̄ from pentachlorotoluene (3:4937) with conc. HNO_3 + Hg see (5); from pentachlorobenzaldehyde (3:4892) with $KMnO_4$ (90% yield) see (1); from *asym.*-tetrachlorophthalyl chloride + Cl_2 via conversion to and subsequent hydrolysis of pentachlorobenzoyl chloride (3:2295) see (3); from 2,3- (3:4650) or 3,4-dichlorobenzoic acid (3:4925) + MnO_2 + fumg. HCl at 180–200° see (4).]

Pentachlorobenzoyl chloride (3:2295), colorless lfts. from alc., m.p. 87° (3), has been prepd. indirectly (see above), but the reaction (if any) of either PCl_5 or $SOCl_2$ on C̄ has never been reported. Upon hydrolysis with alc. KOH the acid chloride yields C̄ (3).

—— Methyl pentachlorobenzoate: pr. from MeOH, m.p. 97° (3). [Prepared from pentachlorobenzoyl chloride + MeOH by 30 hrs. reflux. (3).]

—— Ethyl pentachlorobenzoate: unrecorded.

—— Pentachlorobenzamide: unrecorded.

—— Pentachlorobenzanilide: unrecorded.

3:4910 (1) Lock, *Ber.* 72, 303 (1939). (2) Steiner, *Monatsh.* 36, 827 (1915). (3) Kirpal, Kunze, *Ber.* 62, 2105 (1929). (4) Claus, Bücher, *Ber.* 20, 1627 (1887). (5) Silberrad, *J. Chem. Soc.* 127, 2684 (1925). (6) Eckert, Steiner, *Monatsh.* 36, 187 (1915).

3:4915 4-CHLORO-3-METHYLBENZOIC ACID $C_8H_7O_2Cl$ Beil. IX – 478 IX_1—

M.P.	209-210° cor.	(1)
	209-210°	(2)
	209.5° cor.	(3)
	209° u.c.	(4)
	208°	(5)
	207-208°	(6)
	203°	(7) (8)

Colorless ndls. from hot aq., alm. insol. cold aq.; very spar. sol. even in hot aq.

[For prepn. of Č from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with $K_2Cr_2O_7$ + dil. H_2SO_4 see (8) (1), from 4-chloro-1-ethyl-3-methylbenzene (6) by oxidn. with dil. HNO_3 (1:10) at 100° for 10 hrs. see (6); from 4-chloro-3-methylacetophenone (Beil. VII-307) by oxidn. with alk. $KMnO_4$ see (4); from 4-chloro-3-methyl-ω,ω,ω-trichloroacetophenone (3) see (3), from β-chloroethyl 4-chloro-3-methylphenyl ketone (5) by oxidn. with mixt. of equal pts. conc. HNO_3 and aq. at 100° see (5); from 1,2-*bis*-(4-chloro-3-methylbenzoyl)-1,2-dibromoethane (2) by fusion with NaOH see (2); from 4-amino-3-methylbenzoic acid (Beil. XIV-480) via diazotization and use of Cu_2Cl_2 reactn. see (7).]

Č on fusion with KOH yields (1) 4-hydroxy-3-methylbenzoic acid (Beil. X-225, X_1-(97)], m.p. 173° (1), together with some 4-hydroxyisophthalic acid (Beil. X-502, X_1-(250)].

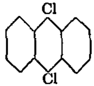
Salts. $Ca\bar{A}_2.3H_2O$ (8), $Ba\bar{A}_2.3H_2O$ (8); both cas. sol. aq.

Č on further oxidn. with $KMnO_4$ yields (1) 4-chlorobenzenedicarboxylic acid-1,3 (4-chloroisophthalic acid) (3:4980).

—— Ethyl 4-chloro-3-methylbenzoate: oil, b.p. 260-265° (8). [From Č in alc. with HCl gas (8).]

3:4915 (1) Jacobsen, *Ber.* 18, 1761-1762 (1885). (2) Conant [illegible] (1925). (3) Houben, Fischer, *Ber.* 64, 2649 (1931). (4) [illegible] 358 (1891). (5) Mayer, Müller, *Ber.* 60, 2281 (1927). (6) [illegible] (1921). (7) Beilstein, Kreusler, *Ann.* 144, 182 (1867). (8) [illegible]

3:4916 9,10-DICHLOROANTHRACENE (*meso*-Dichloroanthracene)



$C_{14}H_8Cl_2$ Beil. V - 664 V_1-(324) V_2-(575)

M.P.	**210°**	(1)
	209–210°	(2) (3)
	209°	(4) (5) (6) (7) (8) (9) (10) (23)
	208–209°	(11) (12)

Yellow ndls. from CCl_4 or C_6H_6 or by sublimation; spar. sol. alc. or ether, eas. sol. C_6H_6.

[For prepn. of $\bar{C}$ from anthracene (1:7285) with Cl_2 in *o*-dichlorobenzene (5) (30) polychlorobenzenes of b.p. 140–170° (4), nitrobenzene (4) (5), or in acetylene tetrachloride (5) (yields: 93–94% (4), 87–88% (5)) see indic. refs. (note that numerous attempts to use this reactn. are given in earlier literature (3) (13) (14) (15) (16) (17) (18) (19) (20) but none is well adapted for pure $\bar{C}$ owing to simultaneous formn. of more highly chlorinated cpds.); from anthracene with SO_2Cl_2 in CCl_4 (7) (11) or in xylene (11) at ord. temp. (yields alm. quant. (7) (11)) see indic. refs. (note, however, that the results are sometimes influenced by the source of anthracene used (11)); for formn. of $\bar{C}$ from anthracene (1:7285) with Cl_2-aq. (21), with S_2Cl_2 (10), or with NOCl in s.t. at 150° or at room temp. in sunlight (22) see indic. refs.; for formn. of $\bar{C}$ from anthracene present in crude phenanthrene during *treatment of latter in* CS_2 *with* Cl_2 see (12).]

[For prepn. of $\bar{C}$ from anthrone (9-hydroxyanthracene) [Beil. VII-473, VII_1-(256)] with 2 wt. pts. PCl_5 in C_6H_6 or without solv. at 100° for 16 hrs. see (2); for formn. of $\bar{C}$ from 9,9,10,10-tetrachloro-9,10-dihydroanthracene (9,10-dichloroanthracene dichloride-9,10) [Beil. V-641, V_1-(309)] by actn. of Zn dust, Cu powder, or phenylhydrazine (3) or on boilg. with anthrone (above) in xylene (6) see indic. refs.; for formn. of $\bar{C}$ from 1,2,3,4-tetrachloro-9,10-dichloroanthracene by htg. with hydrazine hydrate + Cu powder in pyridine (23), or from 9-benzylanthracene with $SOCl_2$ in $CHCl_3$ (24), see indic. refs.; from α-[9,10-dichloroanthracene tetrabromide-1,2,3,4] (see below) by treatment with Zn dust in AcOH or with Cu powder in C_6H_6 see (3).]

[$\bar{C}$ with Cl_2 in *cold* $CHCl_3$ or acetylene tetrachloride gives (17) 9,9,10,10-tetrachloro-9,10-dihydroanthracene (see above); $\bar{C}$ with Cl_2 in C_6H_6 at 60° yields (17) 2,3,9,10-tetrachloro-2,3-dihydroanthracene; $\bar{C}$ in warm $CHCl_3$ or cold C_6H_6 gives (17) a mixt. of these prods.: the end prod. of chlorination of $\bar{C}$ in C_6H_6 at 20° appears (16) (3) to be 1,2,3,4,9,10-hexachloro-1,2,3,4-tetrahydroanthracene [Beil. V-611, V_1-(287)], m.p. 205–207° (3). — $\bar{C}$ with SO_2Cl_2 in nitrobenzene at *100°* yields (25) *2,9,10-trichloroanthracene.*]

$\bar{C}$ adds 2 moles Br_2 giving according to conditions one or the other of two isomeric addn. compds.; i.e., $\bar{C}$ moistened with $CHCl_3$ and treated with 2 Br_2 yields (3) (8) α-[9,10-dichloroanthracene-1,2,3,4-tetrabromide], colorless hexag. pr. from C_6H_6, m.p. 141–142° (3), while $\bar{C}$ with Br_2 vapor gives (3) β-[9,10-dichloroanthracene-1,2,3,4-tetrabromide], ndls. from C_6H_6 (less sol. than α-isomer), m.p. 178–179° (3), 178° (16) (8), 166° (15); both α- and β-isomers with alc. KOH lose 2 HBr (the α- more rapidly than the β-) yielding (3) (8) 2,3-dibromo-9,10-dichloroanthracene, yel. ndls., m.p. 255–256° (3), 251–252° (15) (16) (8).

[$\bar{C}$ in $CHCl_3$ treated with NO_2 gas gives (26) 9,10-dichloro-9,10-dinitro-9,10-dihydroanthracene (very unstable white cryst. on strong cooling) which in boilg. $CHCl_3$ yields anthraquinone (1:9095). — $\bar{C}$ with conc. HNO_3 ($D = 1.43$) in AcOH at 15–18° yields (27) 9,10-dichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII_1-(258)].]

[$\bar{C}$ with fumg. H_2SO_4 (20% SO_3) in nitrobenzene at 12–15° (4) (5) cf. (28) (30) or in benzenesulfonyl chloride below 50° (28), or $\bar{C}$ with $ClSO_3H$ in $CHCl_3$ or H_2SO_4 at 30° (29),

yields 9,10-dichloroanthracenesulfonic acid-2 [Beil. XI$_1$-(44)], cryst. with 2½ H_2O from alc., m.p. 158–159° (4), losing aq. in vac. at 140° to anhydrous acid, m.p. 212° cor. dec. (4) (corresp. sulfonyl chloride, m.p. 221–225° dec., corresp. sulfonamide, m.p. 279°, corresp. sulfonanilide, m.p. 247.8° cor. (4)).] — [For disulfonation of C̄ see (33).]

C̄ is unaffected (13) by boilg. alc. KOH. — [For behavior of C̄ with *pyridine* see (31). — For reactn of C̄ with NaSH in alc. yielding anthranol, anthrone, dianthrone, and other prods. see (32). — For use of C̄ in prepn. of sulfur dyes see (34).]

C̄ on oxidation yields (18) anthraquinone (1:9095).

C̄ like many other anthracene derivs. adds to suitable unsatd. linkages (35) (36) (37) in Diels-Alder fashion: e.g., C̄ with maleic anhydride (1:0625) in nitrobenzene, boiled for 15 min., gives on cooling (50% yield (35)) adduct, colorless pr. from xylene, m.p. 258–259°, from chlorobenzene, m.p. 253° (36); *in this adduct the halogen is stable toward boilg. alc.* KOH (38) (39), but the adduct with $AlCl_3$ in C_6H_6 refluxed 10 min. yields (35) *9,10-diphenylanthracene* [Beil. V-747, V$_1$-(377)], cryst. from toluene, m.p. 248° (35). — C̄ with β-chloropropionic acid (3:0460) (used as source of acrylic acid (1:1020) by loss of HCl) boiled for 8 hrs. in *o*-dichlorobenzene yields an adduct, cryst. from anisole, m.p. 245° (38); the halogen of this adduct is stable toward hydrolysis and is not removed by boilg. with 10% alc. KOH for 40 min. (38) — C̄ does *not* (38) form an adduct with cinnamic acid.

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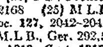
3:4920 3,4,5-TRICHLOROBENZOIC ACID $C_7H_3O_2Cl_3$ Beil. IX - 346
IX$_1$—



M.P. 210–210.5° (1)
203° (2)

Ndls. from aq. alc. — Sublimes in long ndls. — Somewhat volatile with steam. — Eas.

sol. cold alc., ether, acetone; mod. sol. C_6H_6, $CHCl_3$; spar. sol. CS_2, pet. eth.; alm. insol. cold aq.

[For prepn. of $\bar{C}$ from 3,4,5-trichlorobenzaldehyde (3:2440) by oxidn. with alk. $KMnO_4$ see (1); from 3,5-dinitro-4-aminobenzoic acid (chrysanisic acid) [Beil. XIV-445] with fumg. HCl at 200° see (2); for formn. (together with other products) from benzotrichloride (3:6540) + Cl_2 see (3).]

[For study of $Ag\bar{A}$, $Ca\bar{A}_2.6H_2O$, $Ba\bar{A}_2.4H_2O$ see (2).]

The direct nitration of $\bar{C}$ has not been recorded. [However, 3,4,5-trichloro-2-nitrobenzoic acid, ndls. from alc., m.p. 181–181.5° (1), and 3,4,5-trichloro-2,6-dinitrobenzoic acid, m.p. 219–221.5° (1), have both been prepared from the corresponding aldehydes.]

$\bar{C}$ with PCl_5 yields (2) 3,4,5-trichlorobenzoyl chloride, m.p. 36° (2).

—— Methyl 3,4,5-trichlorobenzoate: unrecorded.
—— Ethyl 3,4,5-trichlorobenzoate: from $\bar{C}$ + alc. + HCl (2), ndls., m.p. 86° (2).
Ⓓ 3,4,5-Trichlorobenzamide: from 3,4,5-trichlorobenzoyl chloride + conc. aq. NH_4OH at 100° (2); ndls. from C_6H_6, m.p. 176° (2).
—— 3,4,5-Trichlorobenzanilide: unrecorded.

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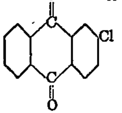
3:4922 2-CHLOROANTHRAQUINONE $C_{14}H_7O_2Cl$ Beil. VII - 787 VII₁-(411)



M.P. 212.4° cor.	(1)	M.P. (Contd.)	208°	(36)
211.0° cor.	(2)		207°	(10) (11)
210° cor.	(3)		206–207°	(12) (13)
210°	(4)		205–207°	(14)
209°	(9)		204.5–205.5°	(15)
209.5°	(5) (6)		204°	(16) (18)
208–209°	(7) (8)		203–204°	(17)

[*See also* 1-*chloroanthraquinone* (3:4480).]

Pale yel. ndls. from C_6H_6, chlorobenzene, or toluene; eas. sol. boilg. C_6H_6, toluene, or AcOH; spar. sol. boilg. alc. — Sublimes in vac.

[For f.p./compn. data and diagram of system $\bar{C}$ + 1-chloroanthraquinone (3:4480) (eutectic, m.p. 143.9–144.2°, contg. about 75% $\bar{C}$) see (5).]

[For use of $\bar{C}$ in coloring oils, fats, and waxes see (19); $\bar{C}$ is widely used as intermediate in prepn. of many dyestuffs, but no general summary can be given here although selected examples occur in the following text.]

[For prepn. of $\bar{C}$ from anthraquinonesulfonic acid-2 [Beil. XI-337, XI₁-(83)] or its Na salt with 25% HCl + $NaClO_3$ at 100° (11) (20) (for use of this method in detn. of mixt. of anthraquinone-α- and β-sulfonic acids or their salts by f.p./compn. curve of resultant mixt. of 1-chloroanthraquinone (3:4480) + $\bar{C}$ see (5)) see indic. refs.; from sodium anthraquinone-2-sulfonate in dil. HCl on exposure to light see (9), from anthraquinonesulfonic acid-2 on boilg. with dil. H_2SO_4 + NaCl + $NaClO_3$ see (21); from anthracenesulfonic

acid-2 [Beil. XI-194, XI_1-(44)] with HCl + $NaClO_3$ at 100° see (22); from anthraquinonesulfonic acid-2 or its Na salt (23) or from anthraquinonesulfonyl chloride-2 (24) with $SOCl_2$ in s.t. at 200–230° see indic. refs.]

[For prepn. of C̄ from *o*-(4-chlorobenzoyl)benzoic acid [Beil. X-750, X_1-(356)] by ring closure with conc. H_2SO_4 at 160–170° (25) (16) (26) (27) (28) (4) (29) (34) (49) in pres. of $AlCl_3$ (30) see indic. refs (for study of influence of conditions see espec. (27) (4) (31)); from *o*-(3-chlorobenzoyl)benzoic acid (32) or from 2-benzoyl-4-chlorobenzoic acid [Beil. X-750, X_1-(356)] (33) by similar ring closure with H_2SO_4 see indic. refs.; from 4-chloro-2-benzoyl-benzoyl chloride on htg. see (33).]

[For prepn. of C̄ from 2-chlorobutadiene-1,3 (chloroprene) (3:7080) + naphthoquinone-1,4 (1:9040) in C_6H_6 see (6); from *α*-chlorocrotonaldehyde (3:8117) + naphthoquinone-1,4 (1:9040) in C_6H_6 with piperidine see (74), from 2-aminoanthraquinone (see below) via diazotization and rapid htg. of diazonium chloride at 150° see (8); from 2-chloroanthraquinonecarboxylic acid-4 by htg. at 286–290° (7) or from 2-chloroanthraquinonecarboxylic acid-5 by htg in s.t. at 310–320° or by distn. of its Ba salt with BaO see (17) of (15); from 2,9,10-trichloro-9-hydroxy-10-nitro-9,10-dihydroanthracene [Beil. VII_1-(258)] in C_6H_6, nitrobenzene, or AcOH by htg at 90–95° see (35); from 2,9,10-trichloroanthracene [Beil. V_1-(325)] (36) or from 2-chloroanthrone-9 (or 10) (12) by oxidn. with CrO_3 see indic. refs.]

[For prepn. of C̄ from 1-chloroanthraquinone (3:4480) by htg. with conc. H_2SO_4 at 200–205° for 9 hrs. see (37).]

[C̄ on reductn. with Zn dust + conc. aq. NH_4OH under reflux yields (18) (37) 2-chloroanthracene [Beil. V_1-(324)], m.p. 217° (37), 215° (18). — C̄ on reductn. with hydrazine hydrate in MeOH/KOH at 10 atm. and 135° for 1½ hrs. in pres. of $Pd/CaCO_3$ cat. yields (38) *bis*-(2,2′-anthraquinonyl) [Beil. VII_1-(495)], m.p. 387–388°. — C̄ on reductn. with Al powder + conc. H_2SO_4 (40) or with Sn + HCl (39) yields a mixt. of 3-chloroanthrone-9, m.p. 156° (38) (corresp. acetate, m.p. 146° (41) (42)), and 2-chloroanthrone-9, m.p. 155° (41) (corresp. acetate, m.p. 143° (41)); this mixt. of chloroanthrones can be sepd. by acetylation with Ac_2O + pyridine and fractional crystn. of the resultant acetates (42). — For use of this reductn. method in prepn. of vat dyes see (43). — For study of oxidn/reductn. potential of C̄ see (13).]

[C̄ with MeOH/KOH in s.t. at 130° yields (44) 2-methoxyanthraquinone [Beil VIII-343, $VIII_1$-(655)], m.p. 196°. — C̄ with 2-hydroxyanthraquinone + NaOAc + Cu powder htd. at 250–260° for 12 hrs. gives (66% yield (45)) di-(2-anthraquinonyl) ether, pale yel. ndls. from pyridine, m.p. 324° (45). — C̄ with K xanthate + Cu powder boiled for 16 hrs. in AmOH gives (56% yield (45) (46) di-(2-anthraquinonyl) sulfide, cryst. from xylene, m.p. 290.5–291° (45). — C̄ with thiosalicylic acid (2-mercaptobenzoic acid) + solid KOH htd. in AmOH at 150° for 8 hrs. gives (77% yield (3)) *S*-(2-anthraquinonyl)thiosalicylic acid [Beil. X_1-(56)], m.p. 278° cor. (3); this prod. on htg. with H_2SO_4 or better with *p*-toluenesulfonyl chloride at 200° (3) (47) ring-closes by loss of H_2O to 1,2-phthalylthioxanthone [Beil. $XVII_1$-(291)], yel. ndls. from AcOH, m.p. 278° cor. (3).]

[C̄ with NaOH + glycerol htd. at 190° is claimed (48) to yield anthraquinone (1:9095). — C̄ with NaOH + $NaClO_3$ htd. 28 hrs. at 195° (49) cf. (50) (51) (52) gives (95% yield (49)) 1,2-dihydroxyanthraquinone (alizarin) (1:9105). — C̄ with NaSH boiled in aq. alc. yields (53) 2-mercaptoanthraquinone [Beil. VIII-346, $VIII_1$-(659)], yel. ndls. from AcOH, m.p. 206° (54). — C̄ with Na_2Se boiled in dil. alc. yields (55) 2-selenomercaptoanthraquinone, but C̄ with Se + NaOAc htd. at 205–210° in a mixt. of trichlorobenzene + tetralin for 8 hrs. yields (56) di-(2-anthraquinonyl) selenide.]

[C̄ with conc. aq. NH_4OH in pres. of Cu salts under press. and at elevated temp. (180–200°) gives (yields: 97.5% (57), 98.6% (2)) (27) (58) (59) (60) 2-aminoanthraquinone [Beil. XIV-191, XIV_1-(449)], red ndls., m.p. 302° (for study of influence of conditions see

(57) (2) (27) (61) (62)). — C̄ with hydrazine hydrate + pyridine in s.t. at 170° for 8 hrs. gives (20% yield (63)) 2-hydrazinoanthraquinone [Beil. XV_1-(200)], or.-yel. ndls. from pyridine, m.p. 228–229° (63).]

[C̄ with 4 moles C_6H_5MgBr in ether yields (64) (65) 2-chloro-9,10-diphenylanthracene, yel. cryst. powder, or. ndls. from AcOH, m.p. 194° (64), 193° (66), 185° (65).]

[For formn. of addn. cpds. of C̄ with $SbCl_5$ in $CHCl_3$ see (10); for formn. of 2-anthraquinonylpyridinium chloride from C̄ + $AlCl_3$ in pyridine see (67).]

[The direct sulfonation of C̄ appears not to have been reported in the scientific literature although C̄ with fumg. H_2SO_4 at 125–130° in pres. of Hg salts cf. (73) as directed is claimed in a patent (68) to yield 2-chloroanthraquinonesulfonic acid-5. — Two monosulfonic acids of C̄ are known, however, although prepared by indirect means; these are 2-chloroanthraquinonesulfonic acid-6 (corresp. sulfonyl chloride, deep yel. ndls. from chlorobenzene, m.p. 202° (69), from C_6H_6, m.p. 202–203° (71)), and 2-chloroanthraquinonesulfonic acid-7 (corresp. sulfonyl chloride, yel. cryst. from C_6H_6, m.p. 205° (70), 200–201° (71), 176° (69)); note that the alkali salts of *both* these acids are almost completely insoluble in aq. (71) and the above anomaly in m.p. of the sulfonyl chlorides may have been due to impure material. — C̄ on htg. with fumg. H_2SO_4 (40% SO_3) at 180° yields (72) a mixt. of sulfonated products which on alk. fusion give 1,2,6-trihydroxyanthraquinone (flavopurpurin) [Beil. VIII-513, $VIII_1$-(741)] and 1,2,7-trihydroxyanthraquinone (anthrapurpurin) [Beil. VIII-516, $VIII_1$-(742)].]

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Ltd., & Loveluck, Thomso [illegible]
1932; *Cent.* **1933**, I 3499. [illegible]
31, 1933; *Cent.* **1933**, II 1764.

(31) Oda, Tamura, *Sci Papers Inst. Phys. Chem.* **32**, 263–273 (1937); *Cent.* **1937**, II 4027; *C.A.* **31**, 8330 (1937). (32) Bailey (to Barrett Co.), U.S. 1,515,325, Nov. 11, 1924; *Cent.* **1925**, I 1014. (33) Egerer, Meyer, *Monatsh.* **34**, 76, 84 (1913). (34) Müller, Kirchner (to I.G.), Ger. 499,587, June 10, 1930; *Cent.* **1931**, I 1675. (35) M.L.B., Ger. 296,019, Jan. 15, 1917; [illegible] 4). (37) Atack, Clough, [illegible] Zink, *J. prakt. Chem.* (2) [illegible] –2551, 2554–2555 (1923). [illegible] Goodway, *J. Chem. Soc* **1930**, 1350. (43) Bayer and Co., Ger. 203,436, Oct. 20, 1908; *Cent* **1908**, II 1756. (44) Bayer and Co., Ger. 229,316, Dec. 13, 1910; *Cent.* **1911**, I 180. (45) Perkin, Sewell, *J. Chem. Soc.* **123**, 3036–3038 (1923). (46) Ullmann-Goldberg, Ger. 255,591, Jan. 10, 1913; *Cent.* **1913**, I 480. (47) Ullmann, Ger. 238,983, Oct. 7, 1911; *Cent.* **1911**, II 1289. (48) Oda, Tamura, Maeda,

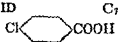
J. Soc. Chem. Ind. Japan **41** (Suppl bindg.), 193–195 (1938); *Cent.* **1939**, I 1360; *C.A* **32**, 7447 (1938). (49) Karpukhin, *Anilinokrasochnaya Prom.* **5**, 317–321 (1935), *Cent.* **1936**, I 2825, *C A* **30**, 7112 (1936). (50) Davies and Scottish Dyes, Ltd , Brit. 174,101, Feb. 16, 1922; *Cent.* **1922**, II 877

(51) Rogers (to National Aniline and Chem. Co.), Brit. 181,673, Aug. 10, 1922; *Cent* **1923**, IV 882. (52) Scottish Dyes, Ltd., & Thomas & Hereward, Brit. 246,529, Feb. 25, 1926, French 591,489, July 4, 1925, Swiss 115,113, June 1, 1926, *Cent* **1926**, II 2949 (53) Bayer and Co., Ger 206,536, Feb. 4, 1909, *Cent.* **1909**, I 1059 (54) Gattermann, *Ann* **393**, 149–155 (1912). (55) Bayer and Co , Ger. 264,911, Sept. 25, 1913, *Cent.* **1913**, II 1351 (56) Perkins (to du Pont Co), U.S. 1,973,773, Sept. 18, 1934, *Cent* **1935**, I 3051 (57) Groggins, Sirton, *Ind. Eng Chem.* **25**, 42–49 (1933). (58) B.A.S.F , Ger 295,624, Dec 11, 1916; *Cent.* **1917**, I 295. (59) Williams (to du Pont Co), U.S 1,775,360, Sept. 9, 1930, *Cent.* **1931**, II 1195 (60) Groggins, U.S. 1,923,618, Aug 22, 1933; *Cent.* **1933**, II 2894, *C A.* **27**, 5339 (1933), U.S. 1,892,302, Dec. 27, 1932, *Cent* **1933**, II 1764, *C.A.* **27**, 1893 (1933).

(61) Vorozhtsov, Nikitin, *J Gen. Chem (U S S R.)* **7**, 2080–2086 (1937), *Cent.* **1938**, I 2355; *C.A.* **32**, 530 (1938) (62) Vorozhtsov, Kobelev, *J. Gen Chem. (U S.S.R)* **9**, 1515–1516 (1939), *C.A.* **34**, 2658 (1940). (63) Möhlau, *Ber.* **45**, 2246 (1912) (64) Barnett, Cook, Wiltshire, *J. Chem. Soc* **1927**, 1728. (65) E. Bergmann, O Blum-Bergmann, *J. Am Chem. Soc.* **59**, 1440 (1937). (66) Ingold, Marshall, *J. Chem Soc* **1926**, 3087 (67) Miegs, Heidenreich (to I.G.), Ger. 593,671, March 5, 1934, *Cent* **1934**, II 848 (68) Whelen (to du Pont Co), U S. 2,074,306, March 16, 1937, *Cent* **1937**, I 4864, *C A* **31**, 3505 (1937). (69) Fierz-David, Andereau, *Helv. Chim. Acta* **10**, 225–227 (1927) (70) Jones, Mason, *J. Chem. Soc* **1934**, 1814.

(71) Goldberg, *J. Chem Soc* **1932**, 73–74, 77 (72) Bayer and Co., Ger 217,552, Jan. 17, 1910, *Cent* **1910**, I 700 (73) Ullmann, Ger. 223,642, June 27, 1910, *Cent* **1910**, II 427. (74) Nicodemus, Vollmann, Schloffer (to I G), Ger. 715,201, Dec 16, 1941, *Cent* **1942**, I 1811, {*C A.* **38**, 2049 (1944)}

3:4925 3,4-DICHLOROBENZOIC ACID $C_7H_4O_2Cl_2$ **Beil. IX - 343**



IX_1-(141)

M.P.	**211–212°**	(1)	M.P.	**204.1°**	(6)
	208–209°	(2) (20)	(*Contd.*)	**203°**	(7)
	206°	(3)		**201–202°**	(8) (19)
	205°	(4)		**201°**	(9)
	201–205°	(5)		**200° cor.**	(10)

Ndls. from aq., alc., 60% alc. (6), C_6H_6 (2) (6), or 30% AcOH (1) (18). — Volatile with steam. — Appreciably more sol. in hot aq. than in cold; very eas. sol. alc.

[For prepn. of C̄ from 3,4-dichlorotoluene (3:6355) by oxidn. (2) with CrO_3 (8) (11), with dil. HNO_3 in s.t. at 130–140° (9) (3), or with $KMnO_4$ (6) see indic. refs.; for prepn. by oxidn. of 3,4-dichlorobenzyl chloride (8) (11), 3,4-dichlorobenzal chloride (3:6876) (8) (11), 3,4-dichlorobenzaldehyde (3:0550) (12), 3,4-dichlorobiphenyl (3:0685) (10), or chlorinated isopropylbenzene (cumene) (5) see indic refs.: for prepn. from benzoic acid (1:0715) by actn. of HCl + $KClO_3$ (11) (20) or $Ca(OCl)_2$ (11) see indicated refs.: for still other misc. methods see Beil. IX-343 + IX_1-(141)]

C̄ is scarcely affected by htg. with fumg. HNO_3 (13) but on soln. in latter and treatment as directed (13) with conc. H_2SO_4 yields 3,4-dichloro-x-nitrobenzoic acid, m.p. 160° (13). [This prod. *may or may not be identical with that of* m p. 165° obtd indirectly (14).]

C̄ with PCl_5 (15) or $SOCl_2$ (16) yields 3,4-dichlorobenzoyl chloride, b.p. 242° (8), 159–160° at 42 mm. (15), 88.0–88.3° (16). [For formn. of this prod. in chlorination of BzCl see (4)]

—— **Methyl 3,4-dichlorobenzoate**: unrecorded.

—— **Ethyl 3,4-dichlorobenzoate**: b p. 202–203° (8). [For study of rate of hydrolysis see (17)]

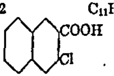
Ⓓ 3,4-Dichlorobenzamide: from 3,4-dichlorobenzoyl chloride + NH_3 (8); m.p. 133° (8); 166–168° (1), 169° (18).

—— 3,4-Dichlorobenzanilide: unrecorded.

3:4925 (1) Gough, King, *J. Chem. Soc.* **1930**, 690–691. (2) Kraay, *Rec. trav. chim.* **49**, 1086 (1930). (3) Wynne, *J. Chem. Soc.* **1936**, 705. (4) Hope, Reilly, *J. Chem. Soc.* **123**, 2476 (1923). (5) Quist, Salo, *Acta Acad. Aboensis Math. et Phys.* **8**, No. 4, 30 pp. (1934); *Cent.* **1934**, II 594–595; **1936**, I 538–540; *C.A.* **29**, 6884 (1935). (6) Bornwater, Holleman, *Rec. trav. chim.* **31**, 228–230 (1912). (7) Pieper, *Ann.* **142**, 306 (1876). (8) Beilstein, Kuhlberg, *Ann.* **152**, 224–234 (1869). (9) Lellmann, Klotz, *Ann.* **231**, 313–314 (1885). (10) Scarborough, Waters, *J. Chem. Soc.* **1926**, 560.

(11) Beilstein, *Ann.* **179**, 283 (1875). (12) Gmelin, Bänziger, *Ber.* **29**, 875 (1896). (13) Claus, Bücher, *Ber.* **20**, 1624 (1887). (14) Ruggli, Zaeslin, *Helv. Chim. Acta* **19**, 434–437 (1936). (15) Cohen, Briggs, *J. Chem. Soc.* **83**, 1213 (1903). (16) Norris, Ware, *J. Am. Chem. Soc.* **61**, 1418–1420 (1939). (17) Blakey, McCombie, Scarborough, *J. Chem. Soc.* **1926**, 2863–2868. (18) Cohen, King, Strangeways, *J. Chem. Soc.* **1930**, 3427. (19) Hodgson, Beard, *J. Chem. Soc.* **1927**, 25. (20) Biswas, Das-Gupta, *J. Indian Chem. Soc.* **19**, 497–498 (1942); *C.A.* **37**, 5709 (1943).

3:4928 3-CHLORONAPHTHOIC ACID-2 $C_{11}H_7O_2Cl$ Beil. IX - 661 IX_1-(278)



M.P. 216.5° (1)
216° (2)
212–213° (3)

Cryst. from MeOH + aq. (2) or from C_6H_6 (3). — Eas. sol. org. solv.

[For prepn. of C̄ from 3-aminonaphthoic acid-2 [Beil. XIV-535, XIV_1-(623)] via diazotization and use of Cu_2Cl_2 reactn. (alm. quant. yield) see (3); from the corresp. acid chloride (below) by hydrolysis with aq. see (1).]

C̄ with Cu bronze refluxed in nitrobenzene for 2 hrs. gives (48% yield (4)) β-naphthoic acid (1:0800), m.p. 185° (4).

[No record can be found of direct conv. of C̄ to the corresp. acid chloride (3-chloro-2-naphthoyl chloride); however, this compd., m.p. 56.5° (1), b.p. 248° at 160 mm. (1), has been obtd. indirectly from 3-hydroxy-2-naphthoic acid (1:0850), with PCl_5 in 49% yield (1); note that 3-hydroxy-2-naphthoic acid with $SOCl_2$ gives instead 3-*hydroxy*-2-naphthoyl chloride, m.p. 96° (5), 94.5° (6), in 82% yield (5).

[For condens. of C̄ with pyrazolanthrone see (8).]

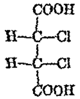
Ⓓ Methyl 3-chloro-2-naphthoate: cryst. from MeOH, m.p. 58–59° (3), 58° (7). [From C̄ in MeOH with conc. H_2SO_4 (88% yield (7)), from C̄ with ethereal diazomethane (3), or from the acid chloride (above) with 5 pts. MeOH (3).] [For reactn. of this ester with 1-aminoanthraquinone see (7).]

Ⓓ Ethyl 3-chloro-2-naphthoate: lfts. from lt. pet. or from alc., m.p. 57–59° (3), 50° (1); b.p. 218–222° at 160 mm. (1), 195–197° at 18 mm. (3), volatile with steam. [From C̄ in EtOH with HCl gas (1) (3).]

Ⓓ 3-Chloro-2-naphthoamide: ndls. from AcOH, m.p. 236–237° (1). [From the acid chloride (above) with conc. aq. NH_4OH (1).]

3:4928 (1) [illegible] 1). (2) Hosaeus, *Ber.* **26**, 668–671 (1893). (3) [illegible] (4) Clemo, Spence, *J. Chem. Soc.* **1928**, 2818. [illegible] rs *Colourists* **56**, 170 (1940). (6) Abrahart, *J.* [illegible] *Ber.* **51**, 22–23 (1918). (8) I.G., Brit. 298,775, Nov. 8, 1928; French 644,589, Oct. 10, 1928.

3:4930 *meso-α,α'*-**DICHLOROSUCCINIC ACID** $C_4H_4O_4Cl_2$ Beil. II - 619
II_1-(267)
II_2-(558)



M.P. 220° cor., dec. (in sealed cap. tube) (1)
- 217–218° (2)
- 214–218° (10)
- 215° u.c. (3)
- 215° dec. (4) (5) (6) (11) (18)
- 213° (7) (16)
- 210° dec. (8)
- 209–213° (9)

[*See also d,l-α,α'-dichlorosuccinic acid* (3:4711).]

Hexag. pr. from aq — C̄ is readily sol. aq. although less so than its *d,l*-isomer; e.g., 100 cc. satd. aq. soln. of C̄ at 0° conts. 12.0 g. C̄ (4); C̄ is eas. sol. alc., ether, acetone or $CHCl_3$; spar. sol. C_6H_6 or lgr.

[For prepn. of C̄ from disodium salt of maleic acid (1:0470) in satd. aq. NaCl soln. with Cl_2 at 0° in dark or diffuse daylight (yields· 74.5% (7), 66% (10), 65% (1)) cf. (16) see indic. refs. (note that as a side reactn. some addn. of HOCl also occurs leading to as much as 7% (1) chloromalic acid): from fumaric acid (1:0895) with excess Cl_2 in s.t. in sunlight for 3–4 days see (6); from *meso-α,α'*-diaminosuccinic acid [Beil. IV-486, IV_1-(901)] in aq. HCl with NOCl or $AgNO_2$ (75% yield) see (3); from *meso-α,α'*-dichlorosuccinyl (di)-chloride (3 9087) by hydrolysis with aq. see (5).]

[For formn. of C̄ from *bis*-acetyl peroxide (9) by decomposition in chloroacetic acid (3 1370) at 85–95° ($CO_2 + CH_4$ are also formed) see (9).]

C̄ behaves as a normal dibasic acid: titration with standard dil. aq. alk. gives Neut. Eq. 93.5. — [For study of acid strength ($K_1 = 361 \times 10^{-4}$ at 20.2°, $K_2 = 9.4 \times 10^{-4}$ at 17.8° (4)) see (4) (8); (18) for study of conductivity see (11).]

[Salts (of metals). $Ag_2\bar{A}$, amorphous ppt. (6) which on boilg with aq. for 10 hrs. yields (12) both *d,l*-tartaric acid (1:0550) and *meso*-tartaric acid (1:0490); $Ca\bar{A}.2H_2O$, eas. sol. aq. and alc. (6), $Sr\bar{A}.H_2O$ (6); $Ba\bar{A}$, very eas. sol. aq., insol. alc. (6); $Zn\bar{A}.3H_2O$ (6); $Cd\bar{A}.3H_2O$, very eas. sol. aq., insol. alc. (6).]

C̄ with cold aq. KOH loses 1 HCl yielding (5) (7) (14) chlorofumaric acid (3:4853); C̄ with NaOAc/AcOH on boilg. (13) (17) or aq. soln. of $Na_2\bar{A}$ on boilg. ½ hr. (12) loses 1 HCl yielding chloromaleic acid (3:3432); C̄ on warming in dil. H_2SO_4 gives both (14) chlorofumaric and chloromaleic acids. [For study of rate of decompn. of C̄ by aq., acids, or alkalies see (7) (8) (15).]

$K_2\bar{A}$ in aq. soln. maintained at neutrality at 100° dec. with formn. (14) of acetaldehyde (1.0100), CO_2 + *meso*-tartaric acid (1:0490).

C̄ with Ac_2O at 150° yields (12) chloromaleic anhydride (3:0280).

The acid chloride (3.9087) corresp. to C̄ is known but is usually obtd. indirectly.

Ⓓ Dimethyl *meso-α,α'*-dichlorosuccinate: m p. 31.5–32° (see 3:0240).

Ⓓ *Diethyl meso-α,α'-dichlorosuccinate*: m.p. 63° (see 3:1364).

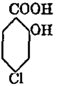
—— Acid salt of C̄ with *dl,-α*-phenylethylamine: tbls. from aq., m.p. 133–134° rap. htg. (13); satd. aq. soln. at 25° conts. 81.4 g./liter (13). [For the corresp. acid salts

of C̄ with the two opt. act. forms of this base see (13); both have m.p. 128–129°, and their satd. aq. solns. at 25° cont. 76.1 g./liter (13).]

3:4930 (1) Kuhn, Wagner-Jauregg, *Ber.* **61**, 501–502, 518–521 (1928). (2) Åminoff, *Arkiv Kemi, Mineral. Geol* **7**, No. 9, 11 (1918); ... uhn, Zumstein, *Ber.* **59**, 485 (1926). (4) K ... 928). (5) Michael, Tissot, *J. prakt. Chem.* (2) ... –215 (1894). (7) Robinson, Lewis, *J. Chem. Soc.* **1933**, 1260–1262. (8) Holmberg, *J. prakt. Chem.* (2) **84**, 148, 152, 164 (1911). (9) Kharasch, Gladstone, *J. Am. Chem. Soc.* **65**, 17 (1943). (10) Terry, Eichelberger, *J. Am. Chem. Soc.* **47**, 1068, 1076–1077 (1925).

(11) Michael, Bunge, *Ber.* **41**, 2912 (1908). (12) Michael, Tissot, *J. prakt. Chem.* (2) **52**, 331–335 (1895). (13) van der Riet, *Ann.* **280**, 229 (1894). (14) Holmberg, *Arkiv Kemi, Mineral. Geol.* **8**, No. 2, 6, 32 (1920); *Cent.* **1921**, I 830; *C.A.* **16**, 2116 (1922). (15) Johansson, *Z. physik. Chem.* **79**, 625–626 (1912). (16) Timmermans, van Laucker, Jaffe, *Bull. soc. chim. Belg.* **48**, 42 (1939). (17) Ashton, Partington, *Trans. Faraday Soc.* **30**, 602 (1934). (18) Holmberg, *Svensk. Kem. Tid.* **24**, 105–109 (1912); *Cent.* **1912**, II 1618; *C.A.* **7**, 80 (1913).

3:4933 4-CHLORO-3-HYDROXYBENZOIC ACID $C_7H_5O_3Cl$ **Beil. S.N. 1068**



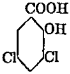
M.P. 219.5–220.5° (1)

Colorless ndls. from aq.

[For prepn. of C̄ from 4-amino-3-hydroxybenzoic acid (1) via diazotization and use of Cu_2Cl_2 reactn. see (1); note that the prod. formerly [Beil. X-143] supposed to have been C̄ is now regarded (1) as probably the 6-chloroisomer (3:4720).]

3:4933 (1) Beyer, *Rec. trav. chim.* **40**, 627 (1921).

3:4935 3,5-DICHLORO-2-HYDROXYBENZOIC ACID $C_7H_4O_3Cl_2$ **Beil. X - 104**
X_1-(48)
(3,5-Dichlorosalicylic acid)



M.P. 220–221°	(1)
219–220°	(2)
219.5°	(3) (10)
219°	(4) (5) (6) (7)
215°	(8)
214°	(9) (11) (12)

Colorless scales or ndls. from aq. alc.; very spar. sol. hot aq., eas. sol. alc., ether; sublimes with partial decomposition.

[For prepn. of C̄ from *o*-hydroxybenzoic acid (salicylic acid) (1:0780) in aq. KOH (3 *moles*) (11) (10), or in aq. KOH (1 mole) (14) (17), or in aq. KOH (2 *moles*) (15) (16), in EtOH (17), in AcOH (12) (10) (2), or in CS_2 susp. (17) with Cl_2 see indic. refs.; with 30% H_2O_2 + HCl (80% yield) see (4); by htg. with $SbCl_5$ see (13). (Note that by most of these methods 5-chloro-2-hydroxybenzoic acid (5-chlorosalicylic acid) (3:4705) may also be formed; from this C̄ may also be sep. via its spar. sol. $Ba\bar{A}_2$ (17).)]

[For prepn. of C̄ from sulfosalicylic acid with Cl_2 in aq. see (8); from K 2,4-dichlorophenolate with CO_2 at 140° see (11); from 3,5-dichlorosalicylaldehyde by oxidn. with alk.

$KMnO_4$ (yield 100%) see (9); from 3,5-dichloro-2-methoxybenzoic acid with 45% HI in s.t. at 120–130° see (3); *from chloral-3,5-dichlorosalicylamide by hydrolysis see* (1).]

$\bar{C}$ on htg. with CaO (17) (7) or at 200° in aniline (18) loses CO_2 yielding 2,4-dichlorophenol (3:0560).

$\bar{C}$ with $FeCl_3$ gives (13) (2) a dark violet color.

[$\bar{C}$ in 60% fumg. H_2SO_4 treated with Cl_2 at 80–90° for 15 hrs. gives (70% yield (19)) 3,5,6-trichlorosalicylic acid, white pl. from aq. alc. or aq. AcOH, m.p. 207° cor. (19); (this with Ac_2O + trace H_2SO_4 gives corresp. acetate, ndls. from lgr., m.p. 129.5° cor. (19)).]

$\bar{C}$ in AcOH treated with fumg. HNO_3 yields (20) 4,6-dichloro-2-nitrophenol, m.p. 122° (20).

$\bar{C}$ with PCl_5 (1 mole) yields (5) (10) 3,5-dichloro-2-hydroxybenzoylchloride (3,5-dichlorosalicyloyl chloride), ndls. from ether + pet. eth., m.p. 79°. [For details on various phosphorus compounds also formed in this reaction see (21).] [Note also existence of anhydride of $\bar{C}$ (from the acid chloride + Ag$\bar{A}$), cryst. from $CHCl_3$, m.p. 186–187° (5) (28).]

[$\bar{C}$ in aq./alc./H_2SO_4 gives (22) on electrolytic reduction 3,5-dichloro-2-hydroxybenzyl alcohol, ndls. from C_6H_6, m.p. 82° (22); for study of prepn. and thermal rearr. of allyl (23), crotyl (23), benzyl (24), and other (25) ethers of $\bar{C}$ see indic. refs.]

Ⓓ **Methyl 3,5-dichloro-2-hydroxybenzoate**: ndls. from alc. or ether, m.p. 150° (15), 147° (5) (26), 143–144° (7) (3), 142° (12). [From Ag$\bar{A}$ + MeI in s.t. at 135° (12), from 3,5-dichlorosalicyloyl chloride (above) with MeOH (5), or from methyl salicylate (1:1750) in AcOH with Cl_2 (26).] [This ester with Ac_2O yields (7) corresp. acetate, ndls. from MeOH, m.p. 57° (7).]

Ⓓ **Ethyl 3,5-dichloro-2-hydroxybenzoate**: cryst. from ether, m.p. 57° (5), 47° (12). [From Ag$\bar{A}$ + C_2H_5I as above (12) (3), from 3,5-dichlorosalicyloyl chloride (above) with EtOH (5), or from ethyl salicylate (1:1755) with Cl_2 (27).]

—— **3,5-Dichloro-2-hydroxybenzamide**: m.p. 209° (11).

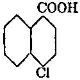
—— **3,5-Dichloro-2-hydroxybenzanilide**: m.p. 134.5° (5) [From 3,5-dichlorosalicyloyl chloride (above) with aniline in ether (5).]

3:4935 (1) Hirwe, Rana, *Ber.* **72**, 1353 (1939). (2) Hirwe, Rana, Gavankar, *Proc. Indian Acad. Sci.* **A-8**, *211 (1938).* (3) *Martini, Gazz. chim. ital.* **29**, *II 62–63 (1899).* (4) Leulier, Pinet, *Bull. soc. chim.* (4) **41**, 1363–1364 (1927). (5) Anschutz, Mehring, *Ann.* **346**, 300–311 (1906). (6) Biltz, Stepf, *Ber.* **37**, 4030 (1904). (7) Zincke, *Ann.* **261**, 252–254 (1891). (8) Datta, Mitter, *J. Am. Chem. Soc.* **41**, 2037 (1919). (9) Dey, Row, *J. Chem. Soc.* **125**, 560 (1924). (10) Earle, Jackson, *J. Am. Chem. Soc.* **28**, 109 (1906).

(11) Tarugi, *Gazz. chim. ital.* **30**, II 487–489 (1900). (12) *Smith, Ber.* **11**, *1225–1227 (1878).* (13) Lossner, *J. prakt. Chem.* (2) **13**, 429–431 (1876). (14) Cahours, *Ann. chim.* (3) **13**, 108–111 (1845); *Ann.* **52**, 341–343 (1844). (15) Lassar-Cohn, Schultze, *Ber.* **38**, 3300 (1905). (16) Ullmann, Kopetschni, *Ber.* **44**, 428 (1911). (17) Hecht, *Am. Chem. J.* **12**, 503–506 (1890). (18) Cazeneuve, *Bull. soc. chim.* (3) **15**, 74 (1896). (19) Farinholt, Stuart, Twiss, *J. Am. Chem. Soc.* **62**, 1239 (1940). (20) Smith, Knerr, *Am. Chem. J.* **8**, 98 (1886).

(21) Anschütz, *Ann.* **454**, 81–82, 105–106 (1927). (22) Mettler, *Ber.* **39**, 2939 (1906). (23) Tarbell, Wilson, *J. Am. Chem. Soc.* **64**, 607–612 (1942). (24) Tarbell, Wystrach, *J. Am. Chem. Soc.* **65**, 2146–2149 (1943). (25) Tarbell, Wystrach, *J. Am. Chem. Soc.* **65**, 2149–2153 (1943). (26) Claisen, *Ann.* **418**, 85 (1919). (27) Cahours, *Ann. chim.* (3) **27**, 461–462 (1849); *Ann.* **74**, 312 (1850). (28) Anschütz, *Ber.* **30**, 223 (1897).

3:4936 4-CHLORONAPHTHOIC ACID-1



$C_{11}H_7O_2Cl$ **Beil. IX - 651**
IX_1—

M.P. 221–223° (2)
210° (1)

Ndls. from alc.; eas. sol. alc. or AcOH; spar. sol. aq., $CHCl_3$, ether, or hydrocarbons.

[For prepn. of C̄ from 4-aminonaphthoic acid-1 [Beil. XIV-533] by diazotization, conversion with CuCN to 4-chloronaphthonitrile (see below), and hydrolysis of the latter by boilg. with a mixt. of 50% AcOH (2 vols.) + conc. H_2SO_4 (1 vol.) see (1); from 1-chloro-4-(chloromethyl)naphthalene, m.p. 78–79° (2), by oxidn. with dil. HNO_3 see (2); or from 1-bromo-4-chloronaphthalene [Beil. V-548, V_2-(448)] by conv. to RMgBr and carbonation see (2).]

C̄ does not react either with conc. NH_4OH at 200° or with $(NH_4)_2CO_3$ at 220° (1).

Salts. *The alk. salts of C̄ are eas. sol. aq.; the calcium, barium, and silver salts are* sparingly sol. aq.; the iron, lead, and copper salts are insol. aq. (1).

—— Methyl 4-chloro-1-naphthoate: unreported.

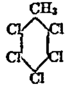
—— Ethyl 4-chloro-1-naphthoate: unreported.

—— 4-Chloro-1-naphthonitrile: long white ndls. from AcOH, m.p. 110° (1).

Ⓓ *p*-Bromophenacyl 4-chloro-1-naphthoate: m.p. 130.5–131° (2).

3:4936 (1) Friedländer, Weisberg, *Ber.* **28**, 1840, 1842–1843 (1895). (2) Horn, Warren, *J. Chem. Soc.* **1946**, 144.

3:4937 2,3,4,5,6-PENTACHLOROTOLUENE (*Eso*-Pentachlorotoluene)



$C_7H_3Cl_5$ Beil. V - 303 V_1-(153) V_2-(234)

M.P. 224.5–225.5°	(1)	B.P. 301° (6)
224–224.5°	(2)	
224°	(3)	
218°	(4) (5) (6) (7)	
217.5° u.c.	(8)	

White ndls. from C_6H_6 or pet. eth. — Spar. sol. hot alc. or ether; spar. sol. cold CS_2 but eas. sol. hot CS_2; sol. at 17° in 22 vols. or at 87° in 3.4 vols. toluene (8). — Sublimes readily. — Closely resembles hexachlorobenzene (3:4939), and the m.p. of mixtures of the two are but very slightly depressed (7) (8); furthermore, soly. of C̄ in C_6H_6 at 4 different temps. is alm. identical with that of hexachlorobenzene (9).

[For studies on dielectric characteristics of C̄ see (9) (10) (11) (12).]

[For prepn. of C̄ from toluene (1:7405) with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 at 100° for ½ hr. as directed (72% yield (8)), or by electrolysis in AcOH/conc. HCl in dark (7), or with Cl_2 in pres. of I_2 followed by further chlorination in pres. of $SbCl_5$ of the fraction boiling above 240° (6) see indic. refs.; for formn. of C̄ from isopropylbenzene (cumene) (1:7440) with Cl_2 in pres. of I_2 + Fe at 0°, or from *p*-cymene (1:7505) with Cl_2 in pres. of I_2 + Fe (1), or from 2-chlorotoluenesulfonyl chloride-4 with Cl_2 in pres. of $SbCl_3$ at 65–70° (4), or from 2,3,4-trichlorotoluene (3:0425) or 2,4,5-trichlorotoluene (3:2100) with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 (8), or from 2,3,4-trichlorobenzal (di)chloride on stdg. (5) see indic. refs.]

[C̄ on further treatment with SO_2Cl_2 + $AlCl_3$ + S_2Cl_2 gives (8) a prod. m.p. 272–274°. — C̄ on fusion and treatment with Cl_2 at 210–230° as directed (13) gives 70–80% yield pentachlorobenzal (di)chloride (3:3590) b.p. 199° cor. at 13 mm. (13).

[C̄ on partial hydrolysis with caustic alk. at 130–140° under press. yields (14) tetrachlorocresol.]

C̄ is unaffected by boilg. fumg. HNO_3 (6), but C̄ on oxidn. with 14.2 wt. pts. conc. HNO_3 ($D = 1.42$) in pres. of 0.1 pt. Hg by boilg. for 150 hrs. (8) yields pentachlorobenzoic acid (3:4910), m.p. 199.5° (8).

C.A. 32, 2548 (1938). (46) van der Linden, *Rec. trav. chim.* 57, olff, *Ber.* 18, 335–337 (1885). (48) Holleman, *Rec. trav. chim.* , *Rec. trav. chim.* 50, 787 (1931). (50) Istrati, *Bull. soc. chim.*

m. Soc. 68, 142 (1946); Dvornikoff (to Monsanto Chem. Co.), .A. 30, 1394 (1936).

ʒOIC ACID $C_7H_5O_2Cl$ Beil. IX - 340

IX_1-(140)

)]	M.P.	238–239°	(23) (70)
1) (2) (3) (4) (64)	(*Contd.*)	238°	(24)
5)		237°	(66) (133)
(6) (7)		236–237°	(25) (126)
(8)		236.5°	(67)
(9) (10)		236°	(26) (27) (28) (29) (51) (54) (61) (72) (77) (86) (156)
(11) (12)			
(13)			
(14) (15) (16) (17)		235.5–236°	(30)
(18) (38) (40)		235–236°	(55)
(19)		235.5°	(31) (53)
(20)		235°	(32) (33) (34) (36)
(21) (22)		234–235°	(56) (71)
		234°	(50)
		233–234°	(69)

— C̄ is almost insol. in cold aq.; e.g., 100 ml. satd. aq soln. at 25° conts. ote that C̄ is thus much less sol. in aq. than *m*-chlorobenzoic acid (3:4392) than *o*-chlorobenzoic acid (3:4150). — At 14–16° 100 ml. satd. soln. of ıs 2 6 g. C̄, in EtOAc 1.6 g. C̄, in 75% AcOH 0.3 g. C̄, in CCl_4 0 04 g. C̄, C̄, in CS_2 0.16 g. C̄ (22). — [For study of soly. of C̄ in acetone (8), C_6H_6 (9) see indic. refs.]

distribution at 25° of C̄ between aq. + toluene or aq. + $CHCl_3$ see (35); of C̄ on charcoal from its solns. in acetone or C_6H_6 see (8); for soly. of C̄ in arious salts (including NaÃ) see (33).]

ıblimed in vac. (19). — C̄ is but very slightly volatile with steam (for details For crystallographic data see (36) (37).]

tems contg. C̄. [For f.p./compn. data on system C̄ + aq. see (38). — For data and diagrams of system C̄ + BzOH (1:0715), eutectic, m.p. 115°, contg. . % C̄, see (22) (16); for f.p./compn. data on systems C̄ + *p*-toluic acid (1:0795) *p*-hydroxybenzoic acid (1:0840) (11), or C̄ + *p*-methoxybenzoic acid (anisic 405) (15) *see indic. refs.*]

/compn data and diagrams on systems C̄ + *o*-chlorobenzoic acid (3:4150), n.p. 132°, contg. abt. 14 mole % C̄, see (22) (39); on system C̄ + *m*-chlorobenzoic 392), eutectic, m p. 140.9°, contg. 20 mole % C̄ (22) (39) (40), see indic. refs.]

p./compn data and diagrams on systems C̄ + *m*-bromobenzoic acid (16), C̄ + benzoic acid (16), C̄ + *p*-nitrobenzoic acid (41), C̄ + *p*-iodobenzoic acid (42) :. refs.]

ary systems contg. C̄. [For influence of addn. of C̄ to the eutectic mixt. of *o*-enzoic acid (3:4150) with *m*-chlorobenzoic acid (3:4392) see (43); *for data on* y system of all three chlorobenzoic acids, eutectic m.p. 104.9°, contg. 48.3 *mole %* + 44.0 mole % *meta* + 7.7 mole % *para* isomers, see (39).]

$+ Cl_2 +$ anhyd. $FeCl_3$ at 125° (33), cf. (34); from various addn. prods. of chlorine with trichloro- (35), tetrachloro- (36), or pentachloro- (37) benzenes usually by means of MeOH/NaOH, from 2,3,5,6-tetrachloro-*N*-nitroaniline, 2,3,5,6-tetrachloro-*N*-nitroacetanilide, or 2,3,5,6-tetrachloro-4-nitro-*N*-nitroaniline in boilg. AcOH + conc. HCl (8), from tetrachlorophthalyl *sym*-dichloride or from pentachlorobenzoyl chloride on distn. (38).]

C̄ with H_2 over Ni at 270° gives (39) C_6H_6, chlorobenzene, dichlorobenzene, trichlorobenzene, etc. — C̄ in boilg. alc. with large excess of Na is completely dehalogenated (40).

C̄ is unattacked by ICl in s.t. at 300° (41) and does *not* react with MeMgI or with MeMgBr in ether even on long boilg. (42).

[C̄ with liq. Cl_2 in s.t. in sunlight yields (37) by addn. both decachlorocyclohexane, m.p. 92°, and dodecachlorocyclohexane, m.p. in sealed cap. tube 285°. — C̄ with F_2 in CCl_4 soln. at 0° yields (43) small amts. of both hexachlorotetrafluorocyclohexene, $C_6Cl_6F_4$, m.p. 113–114°, and hexachlorohexafluorocyclohexane, $C_6Cl_6F_6$, m.p. 94–96°. — C̄ in vapor phase with F_2 in pres. of Cu gives a mixt. of 12 individual prods. (44).]

C̄ with aq. NaOH at 135–138° and 11–12 atm. for 3–4 hrs. (14) or with excess 5–15% soln. of NaOH in MeOH at 135° under press. (45) or C̄ with NaOH in EtOH in s.t. at 150–160° (47) or in dry glycerol at 250–280° (47) gives (80% yield (14)) sodium salt of pentachlorophenol (3:4850). — C̄ with MeOH/NaOH in ethyl methyl ketone soln. at b.p. for ½ hr. gives (43% yield (46)) methyl pentachlorophenyl ether, ndls. from alc., m.p. 108–109°. [For studies of kinetics of reactn. of C̄ with MeOH/NaOH in s.t. at 151° (2), at 176° (48), at 180° (48), at 183° (49) see indic. refs.; of C̄ with EtOH/NaOH or with NaOEt soln. at 175° see (2).]

C̄ on boilg. with mixt. of fumg. HNO_3 + conc. H_2SO_4 gives (50) tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).

[illegible] 2). (2) Clark, Crozier, *Trans.* [illegible] 4. 20, 388 (1926). (3) Pollak, [illegible] Beilstein, Kuhlberg, *Ann.* 150, [illegible] (1927). (6) Pollak, Gebauer- [illegible] 367 (1900). (8) Peters, Rowe, [illegible], *J. prakt. Chem.* (2) 158, 2–4 (1941). (10) Smyth, Lewis, *J. Am. Chem. Soc.* 62, 950 (1940).

(11) van der Linden, *Rec. trav. chim.* 57, 415 (1938). (12) Silberrad, *J. Chem. Soc.* 121, 1021 (1922). (13) Jungfleisch, *Ann. chim.* (4) 15, 287–291 (1868). (14) Troitskii, Voronina, *Org. Chem. Ind. (U.S.S.R.)* 7, 240–241 (1940); *C.A.* 35, 3989 (1941). (15) Krafft, *Ber.* 9, 1087 (1876). (16) Ruoff, *Ber.* 9, 1486 (1876). (17) Wheeler, *J. Am. Chem. Soc.* 42, 1844 (1920). (18) Lonsdale, *Proc. Roy. Soc. London*, A-133, 536–552 (1931). (19) Plummer, *Phil. Mag.* (6) 50, 1214–1220 (1925). (20) Cameron, Thomas, et al., *J. Path. Bact.* 44, 281–296 (1937).

(21) "Chemia" Ungarische Chem. Ind. & von Dalmady, Ger. 389,778, Feb. 7, 1924; Austrian 95,732, Jan. 25, 1924; *Cent.* 1924, I 2801. (22) I.G., French 701,032, March 10, 1931; *Cent.* 1931, II 618. (23) ter Meulen, Heslinga, *Rec. trav. chim.* 42, 1095 (1923). (24) Graebe, *Ann.* 263, 30 (1891). (25) Roberts Co. & Silberrad, Brit. 193,200, March 15, 1923; *Cent.* 1925, I 904. (26) Huntress, Carten, *J. Am. Chem. Soc.* 62, 513 (1940). (27) Simons, Bond, McArthur, *J. Am. Chem. Soc.* 62, 3478 (1940). (28) Davis, McLean, *J. Am. Chem. Soc.* 60, 720–722 (1938). (29) van der Linden, *Rec. trav. chim.* 57, 415–416 (1938). (30) Müller, Hönn, *J. prakt. Chem.* (2) 133, 289–290 (1932).

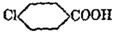
(31) Consortium für Elektrochem. Ind., French 814,423, June 23, 1937; *Cent.* 1937, II 3953. (32) I.G., French 837,741, Feb. 20, 1939, *Cent.* 1939, II 228. (33) Fierz-David, Stähelin, *Helv. Chim. Acta* 20, 1458–1461 (1937). (34) van der Linden, *Rec. trav. chim.* 57, 342–344 (1938). (35) van der Linden, *Rec. trav. chim.* 55, 317–320 (1936). (36) van der Linden, *Rec. trav. chim.* 55, 421–430 (1936). (37) van der Linden, *Rec. trav. chim.* 55, 569–573 (1936). (38) Kirpal, Kunze, *Ber.* 62, 2104–2105 (1929). (39) Mailhe, *Cent.* 1921, III 467. (40) Stepanov, *J. Russ. Phys.-Chem. Soc.* 37, 15 (1905); *Cent.* 1905, I 1273.

(41) Krafft, Merz, *Ber.* 8, 1303 (1875). (42) Durand, Hsün, *Compt. rend.* 191, 1460 (1930). (43) Bigelow, Pearson, *J. Am. Chem. Soc.* 56, 2773–2774 (1934). (44) Fukuhara, Bigelow, *J. Am. Chem. Soc.* 60, 427–429 (1938). (45) Smith, Litvak (to Dow Chem. Co.), U.S. 2,107,650,

Feb. 8, 1938; *Cent.* 1938, I 3821; *C.A.* 32, 2548 (1938). (46) van der Linden, *Rec. trav. chim.* 57, 787–788 (1938). (47) Weber, Wolff, *Ber.* 18, 335–337 (1885). (48) Holleman, *Rec. trav. chim.* 39, 749 (1920). (49) de Crauw, *Rec. trav. chim.* 50, 787 (1931). (50) Istrati, *Bull. soc. chim.* (3) 3, 184–186 (1890).

(51) Dvornikoff, *J Am Chem Soc* 68, 142 (1946); Dvornikoff (to Monsanto Chem. Co.), U S. 2,028,383, Jan. 21, 1936; *C.A.* 30, 1394 (1936).

3:4940 *p*-CHLOROBENZOIC ACID $C_7H_5O_2Cl$ Beil. IX - 340 IX_1-(140)



M.P. [245°	(160)]	M.P. (*Contd.*) 238–239°	(23) (70)
243°	(1) (2) (3) (4) (64)	238°	(24)
243° in s.t.	(5)	237°	(66) (133)
242.5–243.5°	(6) (7)	236–237°	(25) (126)
241.7°	(8)	236.5°	(67)
241.5°	(9) (10)	236°	(26) (27) (28) (29) (51) (54) (61) (72) (77) (86) (156)
241°	(11) (12)	235.5–236°	(30)
240–241°	(13)	235–236°	(55)
240°	(14) (15) (16) (17) (18) (38) (40)	235.5°	(31) (53)
239.7°	(19)	235°	(32) (33) (34) (36)
239° cor.	(20)	234–235°	(56) (71)
239°	(21) (22)	234°	(50)
		233–234°	(69)

Cryst. from alc. — C̄ is almost insol. in cold aq.; e.g., 100 ml. satd. aq. soln. at 25° conts. 0.0068 g. C̄ (33); note that C̄ is thus much less sol. in aq. than *m*-chlorobenzoic acid (3:4392) and far less sol. than *o*-chlorobenzoic acid (3:4150). — At 14–16° 100 ml. satd. soln. of C̄ in acetone conts. 2.6 g. C̄, in EtOAc 1.6 g. C̄, in 75% AcOH 0.3 g C̄, in CCl_4 0 04 g. C̄, in C_6H_6 0.017 g. C̄, in CS_2 0.16 g. C̄ (22). — [For study of soly. of C̄ in acetone (8), C_6H_6 (8) (9), heptane (9) see indic refs.]

[For study of distribution at 25° of C̄ between aq. + toluene or aq. + $CHCl_3$ see (35); for adsorption of C̄ on charcoal from its solns. in acetone or C_6H_6 see (8); for soly. of C̄ in aq. solns. of various salts (including NaÃ) see (33).]

C̄ can be sublimed in vac. (19). — C̄ is but very slightly volatile with steam (for details see (10)). — [For crystallographic data see (36) (37).]

Binary systems contg. C̄. [For f.p./compn. data on system C̄ + aq. see (38). — For f.p./compn. data and diagrams of system C̄ + BzOH (1:0715), eutectic, m.p. 115°, contg. about 10 wt % C̄, see (22) (16); for f p./compn. data on systems C̄ + *p*-toluic acid (1:0795) (11), C̄ + *p*-hydroxybenzoic acid (1.0840) (11), or C̄ + *p*-methoxybenzoic acid (anisic acid) (1:0805) (15) see indic. refs.]

[For f.p./compn. data and diagrams on systems C̄ + *o*-chlorobenzoic acid (3:4150), eutectic, m.p. 132°, contg. abt [illegible] acid (3:4392), eutectic, m.p. [illegible]

[For f.p./compn. data and [illegible] *p*-bromobenzoic acid (16), C̄ [illegible] (41), C̄ + *p*-iodobenzoic acid (42) see indic. refs.]

Ternary systems contg. C̄. [For influence of addn. of C̄ to the eutectic mixt. of *o*-chlorobenzoic acid (3:4150) with *m*-chlorobenzoic acid (3:4392) *see* (43); *for data on* ternary system of all three chlorobenzoic acids, eutectic m.p. 104.9°, contg. 48.3 mole % *ortho* + 44.0 mole % *meta* + 7.7 mole % *para* isomers, see (39).]

Miscellaneous. [For study of fate of C̄ in animal organism see (44) (45) (46) (47); note that conjugation with glycine to yield the expected *N*-(*p*-chlorobenzoyl)glycine (*p*-chlorohippuric acid) [Beil. IX-341], m.p. 143° (45), does occur. — For study of toxicology of C̄ see (46) (48). — Note that sodium salt of C̄ (see also below) is widely used under name "Mikrobin" as preservative. — For use of C̄ as vulcanization regulator see (49).]

Preparation. [For prepn. of C̄ from *p*-chlorotoluene (3:8287) by oxidn. with boilg. 5% aq. $KMnO_4$ (60% yield (51)) (22) (50) (52) (53) (133), with MnO_2 + H_2SO_4 (100% yield (51)), with CrO_3 (54), with dil. HNO_3 in s.t. at 140–145° for ½ hr. (55) or at 115–120° for 5–6 hrs. (56) see indic. refs.; from *p*-chlorotoluene (3:8287) by oxidn. with air in the pres. of various catalysts (57), or at 235–240° and 50–60 atm. press. in pres. of FeO.OH (58), or in aq. alk. at 260° under press. (59) see indic. refs.; for formn. of C̄ from *p*-chlorotoluene (3:8287) by electrolytic oxidn. (2) (60), by action of NOCl (30), or by long exposure to I_2 + aq. in light (28) see indic. refs.]

[For prepn. of C̄ from *p*-chloroacetophenone (3:6735) by oxidn. with alk. $KMnO_4$ (61), with $CrO_3/AcOH/H_2SO_4$ (95% yield (7)), with Cl_2 + NaOH(NaOCl) in aq. MeOH (93% yield (62)), by liquid phase cat. oxidn. with air in pres. of MnO_2 (91% yield (6)) see indic. refs.; for formn. of C̄ from *p*-chloroacetophenone (3:6735) with NOCl see (63).]

[For formn. of C̄ from 4-chloro-isopropylbenzene (*p*-chlorocumene) (3:8705) by oxidn. with HNO_3 (64) (23), from 2,4′-dichlorobiphenyl (3:0670) (65) or from 4,4′-dichlorobiphenyl (3:4300) (66) by oxidn. with CrO_3/AcOH, from benzal-4-chloroacetophenone (24) by oxidn. with $KMnO_4$ in pyridine (90% yield (24)) see indic. refs.]

[For formn. of C̄ from *p*-chlorobenzaldehyde (3:0765) by oxidn. with $KMnO_4$ (67) (68) (69) (70) or CrO_3 (67) or even slowly by air see indic. refs.; from *p*-chlorobenzaldehyde copper during recrystn. (presumably as a result of oxidn. by air) see (31).]

[For prepn. of C̄ from *p*-chlorobenzonitrile [Beil. IX-341, IX_1-(140)] by hydrolysis with 75% H_2SO_4 (71), from *p*-chlorobenzoyl chloride (3:6550) by hydrolysis with aq., from *p*-chlorobenzotrichloride (3:6825) by hydrolysis, e.g., with aq. in s.t. at 200° (72) or with aq. alk., alk. carbonates, or alk.-earth carbonates (73) (note also formn. of C̄ as by-prod. of prepn. of *o*-chlorobenzaldehyde from *o*-chlorotoluene presumably due to hydrolysis of some *p*-chlorobenzotrichloride (81)), from *p*-chlorobenzal (di)chloride (3:6700) with CrO_3 (74) or on boilg. with aq. for 20 hrs. followed by oxidn. with $KMnO_4$ (85% yield (17)); from a mixt. of *p*-chlorobenzotrichloride + *p*-chlorobenzal (di)chloride by hydrol. with 70% H_2SO_4 or 80% AcOH or 5% NaOH at 90–100° in stream of air to effect immediate oxidn. (75) see indic. refs.]

[For prepn. of C̄ from 2-(*p*-chlorobenzoyl)benzoic acid [Beil. X-750, X_1-(356)] by hydrolytic cleavage with aq. + CaO under press. at 325° (93% yield (7)), or from *p*-chlorobromobenzene via conversion to *p*-chlorophenyl lithium bromide (76) or to *p*-chlorophenyl magnesium bromide (77) and subsequent carbonation (90% yield (76)) or from chlorobenzene (3:7903) with $AlCl_3$ + CO_2 at 100° and 60 atm. press. (82) see indic. refs.]

[For formn. of C̄ from benzoic acid (1:0715) with alk. NaOCl (20) cf. (78) or $Ca(OCl)_2$ (79) cf. (25), or from 4-chlorophthalic acid (3:4390) by cat. monodecarboxylation (80), see indic. refs.]

[For formn. of C̄ from di-(*p*-chlorobenzoyl) peroxide by htg. (2) (3), from *p*-aminobenzoic acid via diazotization and use of Cu_2Cl_2 reaction (82% yield (83)), from *p*,*p*′-diazoaminobenzoic acid (diazoaminobenzene-4,4′-dicarboxylic acid) [Beil. XVI-728] with conc. HCl (84), from *p*-chloroisonitrosoacetophenone with warm Ac_2O (21), from *p*-chlorophenacyl bromide by conv. to quaternary salt with quinoline and treatment with aq. NaOH (18), from *p*-borobenzoic acid with hot aq. $CuCl_2$ (26), from di-(*p*-chlorobenzoyl)butane on pyrolysis at 255–265° for 24 hrs. (85), from ethyl *p*-chlorophenyl-azo-carboxylate during oxidn. with H_2O_2 in AcOH (29), from *p*-hydroxybenzoic acid (1:0840) with PCl_5 followed by aq. (86) (87), or from treatment with aq. of the product from *p*-nitrotoluene with

$SOCl_2$ in s.t. at 200–220° (88), *p*-toluenesulfonyl chloride with $SOCl_2$ in s.t. at 230–250° (88), or sodium *p*-toluenesulfonate in chlorobenzene with $SOCl_2$ in s.t. at 250–260° (89) see indic. refs.]

Chemical behavior. No specific account of reduction of $\bar{C}$ to benzoic acid appears to be on record; note, however, detn. of chlorine in $\bar{C}$ by use of Na + alc. (90). — $\bar{C}$ on reduction with formic acid at 250–260° in pres. of TiO_2 gives *p*-chlorobenzaldehyde (3:0765) (89% yield on $\bar{C}$ consumed, or 41% on $\bar{C}$ used (91)). — $\bar{C}$ on electrolytic reduction in alc / H_2SO_4 gives (92) *p*-chlorobenzyl alcohol [Beil. VI-444, VI_1-(222)], m p. 73°, b.p. 234° (92); note proximity of m p. of this prod to that (72°) of corresp. prod. obtd. by similar reduction of *o*-chlorobenzoic acid (3:4150). — For study of reduction of $\bar{C}$ with H_2 + Ni in aq. alk. at ord. temp see (93).

[$\bar{C}$ on electrolytic oxidn. in $AcOH/H_2SO_4$ gives (2) 4-chloro-2-hydroxybenzoic acid (4-chlorosalicylic acid) (3:4908).]

$\bar{C}$ behaves normally as a monobasic acid; e.g, $\bar{C}$ on titration with standard dil. aq. alk. gives Neut. Eq. 156.5; ionization constant at 25° is 0.93×10^{-4} (94), 0.78×10^{-4} (95), 1.04×10^{-4} (96) cf. (97) (12). — [For study of acid strength of $\bar{C}$ in various alcohols see (98) (99) (100) (13) (101) (27).—For soly. of $\bar{C}$ in aq. solns. of various salts (including $Na\bar{A}$) see (33). — For sepn. of $\bar{C}$ from *o*-chlorobenzoic acid (3:4150) by use of difference in acid strength see (102).]

Salts of inorganic bases. $NH_4\bar{A}$ (103). — Hydroxylamine salt; m.p. 130° (104). — $Na\bar{A}$: widely used as food preservative under name " Mikrobin "; for prepn. from $\bar{C}$ + Na phenolate see (105); for study of influence on enzymes see (106) (107); for study of use as preservative see (108); for studies of detection and/or detn. in foods see (109) (110) (111) (112) (113) (114); forms liquid cryst. on fusion (115).

$Ag\bar{A}$, sol. in hot aq (50) (1 l. satd. aq. soln. at 20° conts. 1.08 g. (118)). (Note that this salt (1 mole) with I_2 (2 equivalents) in dry C_6H_6 refluxed 15–18 hrs. yields (116) phenyl *p*-chlorobenzoate, m p. 100° + CO_2 + AgI, and that analogous behavior is shown to lesser degree by corresp. salt of *m*-chlorobenzoic acid (3:4392) but *not* by corresp. salt of *o*-chlorobenzoic acid (3:4150).)

$Ca\bar{A}_2.3H_2O$ (25), 1 l. satd. aq. soln. at 20° conts. 7.37 g. (118). — $Ba\bar{A}_2.3\frac{1}{2}H_2O$ (66); $Ba\bar{A}_2.4H_2O$ (34); $Ba\bar{A}_2.H_2O$ (118); 1 l. satd. aq. soln. of latter at 20° conts. 1.09 g. $Ba\bar{A}_2.H_2O$ (118) (for use of Ba salt in sepn. of the three isomeric chlorobenzoic acids see (43)). — $Cd\bar{A}_2.2H_2O$ (117); 1 l. satd. aq. soln. at 20° conts. 7.79 g. (118). — For similar data on salts of $\bar{C}$ with other heavy metals see (118) (119). — For study of various metal ions as precipitants for $\bar{C}$ see (120).

Salts of organic bases. $\bar{C}$ with equiv. amt. benzylamine in boilg. EtOAc followed by evapn. of solvent yields (121) benzylammonium *p*-chlorobenzoate, m p. 157.4–158.4° u.c., 160.3–161.3° cor., Neut. Eq. 263 6. — $\bar{C}$ similarly treated with α-phenylethylamine yields (121) α-phenylethylammonium *p*-chlorobenzoate, m.p. 150.0–151.0° u c., 152.2–153.2° cor., Neut. Eq. 277.6.

$\bar{C}$ (1 mole) in alc. mixed with codeine (1 mole), m.p. 155°, htd several minutes, solvent evapd. and resultant sirup recrystd. from aq., yields (122) codeine *p*-chlorobenzoate, $C_{18}H_{21}O_3N.\bar{C}$, m.p. 162° on " Maquenne block "; note that this value although close to that (166°) of codeine *p*-bromobenzoate is widely different from and higher than those for the corresp. salts of either *o*-chlorobenzoic acid (3:4150) or *m*-chlorobenzoic acid (3:4392) which are 134° and 96° respectively. — $\bar{C}$ (1 mole) in alc. (or $CHCl_3$) with strychnine (1 mole) in alc., boiled for a few minutes, then cooled, yields (123) strychnine p-chlorobenzoate, $C_{21}H_{22}O_2N_2.\bar{C}$, m.p. 251° on " Maquenne block "; note that the m p. of this salt is far higher than the corresp. products from similar treatment of either the *o*- or *m*- isomers, which are 170° and 185°, respectively.

$\bar{C}$ with alcohols gives by conventional processes the corresp. esters: for details on methyl

p-chlorobenzoate (3:0535) or on ethyl p-chlorobenzoate (3:6750) see these compds. — [For study of rate of esterification of C̄ with MeOH (124) (125) (126), with EtOH (126) (1) (127), with cyclohexanol (128) see indic. refs.]

C̄ with oxalyl (di)chloride (3:5060) refluxed in C_6H_6 (129), or NaĀ htd. with p-chlorobenzoyl chloride (3:6550) (130) gives (50% yield (130)) p-chlorobenzoic acid anhydride, ndls. from dil. acetone or C_6H_6, m.p. 193–194° (129) (131), 194.8° (130), 191.5° (132); note that this prod. may also form in various other reactions involving C̄, especially in pres. of tertiary bases or Na_2CO_3 cf. (131) (132).

C̄ with PCl_5 (133) (50) (45) (132), with $SOCl_2$ (134) (135) (136), with $SOCl_2$ + $AlCl_3$ (137), or with p-chlorobenzotrichloride (3:6825) + $ZnCl_2$ (138) gives p-chlorobenzoyl chloride (3:6550).

[C̄ with chlorobenzene (3:7903) + $AlCl_3$ refluxed 5½ hrs. gives (98% yield (7)) a mixt. consisting mainly of 4,4′-dichlorobenzophenone (3:4270) accompanied by a small proportion of 2,4′-dichlorobenzophenone (3:1565).]

[C̄ with KCN + CuCN in aq. alc. htd. in s.t. at elevated temp. (139) or C̄ (as KĀ) with aq. KCN + CuCN refluxed 8–10 hrs. under H_2 in quartz flask exposed to ultra-violet light (140) gives (70% yield (140)) terephthalic acid (1:0910).]

Substitution of nucleus of C̄. C̄ on mononitration, e.g., with HNO_3 (D = 1.6) on warming until soln. occurs (141), or with 10 wt. pts. HNO_3 (D = 1.5) at 55–60° for 10 minutes (142), or with 4 vols. HNO_3 (D = 1.5) warmed until soln. occurs (143), followed by pouring into aq. gives (yields: 97% (141), 96% (142), 90% (143)) 4-chloro-3-nitrobenzoic acid [Beil. IX-402, IX_1-(165)], cryst. from hot aq., m.p. 184° (142), 182° cor. (141), 180° (143). — [Note that boilg. conc. HNO_3 (D = 1.42) has no action (143) on C̄; that the crude mononitration prod. sometimes (143) contains a small amt. of p-chloronitrobenzene, m.p. 82°; and that the other possible mononitration isomer, viz., 4-chloro-2-nitrobenzoic acid [Beil. IX-401, IX_1-(165)], m.p. 140°, is *not* formed in appreciable amt. by direct nitration of C̄.]

C̄ on dinitration, e.g., with 20 wt. pts. conc. H_2SO_4 + 3.3 wt. pts. KNO_3 at 140° for 1½ hrs. (144), or with 12½ wt. pts. conc. H_2SO_4 + 2.4 wt. pts. fumg. HNO_3 (D = 1.5) at 135–140° for 2 hrs. (145), then poured into aq., gives (yields: 95% (144), 82% (145)) 4-chloro-3,5-dinitrobenzoic acid [Beil. IX-416], pr. from C_6H_6, m.p. 159° (144) (145). For use in detection of C̄ see (161). — [Note that none of the three other isomeric 4-chlorodinitrobenzoic acids has ever been reported.]

[C̄ on sulfonation with SO_3 in fumg. H_2SO_4 (52) (146) (147) gives 4-chloro-3-sulfobenzoic acid [Beil. XI-387].]

—— Methyl *p*-chlorobenzoate: m.p. 43° (see 3:0535).

—— Ethyl *p*-chlorobenzoate: oil, b.p. 238° (see 3:6750).

Ⓓ *p*-Nitrobenzyl *p*-chlorobenzoate: m.p. 130° (148). [From C̄ (as NaĀ) with p-nitrobenzyl bromide (m.p. 99°) in boilg. alc. (148).]

Ⓓ Phenacyl *p*-chlorobenzoate: m.p. 89.5° (149), 87.6° (32). [From C̄ as (NaĀ) with phenacyl bromide (m.p. 50°) in boilg. alc. (98% yield (32)). — Note that the m.p. of this prod. is only slightly higher than that (85.5°) of the corresp. prod. similarly obtd. from o-chlorobenzoic acid (3:4150).]

—— *p*-Chlorophenacyl *p*-chlorobenzoate: unreported.

Ⓓ *p*-Bromophenacyl *p*-chlorobenzoate: m.p. 126° (32). [From C̄ (as NaĀ) with p-bromophenacyl bromide (m.p. 109°) in boilg. alc. (80% yield (32)).]

—— *p*-Iodophenacyl *p*-chlorobenzoate: unreported.

Ⓓ *p*-Phenylphenacyl *p*-chlorobenzoate: m.p. 160° cor. (150). [From C̄ (as NaĀ) with p-phenylphenacyl bromide (m.p. 126°) in boilg. alc. (150). — Note that m.p. of this prod. is only slightly higher than that (154°) of corresp. prod. similarly obtd. from m-chlorobenzoic acid (3:4392).]

—— *S*-Benzylthiuronium *p*-chlorobenzoate: unreported.

D *S*-(*p*-Chlorobenzyl)thiuronium *p*-chlorobenzoate: cryst. from dioxane, m.p. 173° cor. (151). [From Ĉ (as NaÃ or KÃ) in aq. with 1 equiv. of *S*-(*p*-chlorobenzyl)-thiuronium chloride, m.p. 197° (10% in alc.) (151).]

D *S*-(*p*-Bromobenzyl)thiuronium *p*-chlorobenzoate: m.p. 163° cor. (152). [From Ĉ (as NaÃ or KÃ) in aq. with 1 equiv. of *S*-(*p*-bromobenzyl)thiuronium bromide (m.p. 213°) in alc. (152). — Note that m.p. of this prod. is only slightly lower than that (165° cor.) of the corresp. prod. similarly obtd. from *o*-chlorobenzoic acid (3:4150).]

D *p*-Chlorobenzamide: ndls. from aq. or ether, m.p. 180° (153), 179° (154), 179° (67), 178.5° cor. (155), 175° (71). [From Ĉ by refluxing with AcOH + $(NH_4)_2CO_3$ (yield 80% (153), 51% (154)); from *p*-chlorobenzoyl chloride (3:6520) with conc. aq. NH_4OH (50) (155) (67), or from *p*-chlorobenzonitrile [Beil. IX-341, IX_1-(140)] by hydrolysis with hot conc. HCl (71).]

D *p*-Chlorobenzhydrazide: ndls. from hot aq., m.p. 163° (157), 162-163° (156). [From ethyl *p*-chlorobenzoate (3:6730) with alc. hydrazine hydrate on b.p. (yield 87% (156)); for use of this prod. as reagt. for identification of aldehydes and ketones see (156).]

—— *N*-(*p*-chlorobenzoyl)-*N'*-phenylhydrazine: unreported.

D *p*-Chlorobenzanilide: ndls. from alc., m.p. 194-195° (158), 194° (70), 193° (159). [From *p*-chlorobenzoyl chloride (3:6520) with aniline (2 moles) (70); also from *p*-(4-chlorobenzophenone oxime) by Beckmann rearr. (159). Note that the m.p. of this prod. is almost the same as that (192-193°) of the isomeric benz-*p*-chloroanilide [Beil. XII-612, XII_1-(306)].]

—— *p*-Chlorobenz-*p*-toluidide: unreported.

—— *p*-Chlorobenz-α-naphthalide: unreported.

—— *p*-Chlorobenz-β-naphthalide: unreported.

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M.P. 236-237° (1)
236° (2)
235-236° (3)
234° (13)
232° (4)
230-232° (5)
230-231° (6)
230° (7) (20)

[*See also tetrachlorobenzoquinone-1,4 (chloranil)* (3:4978).]

Colorless scales or ndls. from C_6H_6; solvated pr. from AcOH losing solvate in air (2) (8). — For crystallographic data see (9). — Č sublimes with partial decompn. (10); for study of sublimation pressure see (11).

Č is insol. aq.; almost insol. C_6H_6, CCl_4, CS_2; eas. sol. alc., ether; spar. sol. AcOH.
[For study of ht. of formn. of Č see (12); for studies of heat of combustion see (13) (14).]
[For patent on use of Č as vulcanization accelerator see (15).]

PREPARATION OF Č

From tetrachlorobenzoquinone-1,4. For prepn. of Č from chloranil (3:4978) by reduction with various reagents see the following. [For use of aq. SO_2 see (10) (16) (note, however, that this reduction is so slow that it has been used (18) as a method of sepn. of 2,3,5-trichlorobenzoquinone-1,4 (3:4672) from tetrachlorobenzoquinone-1,4 (3:4978), and also that during the process substantial amounts of trichlorohydroquinonesulfonic acid and of dichlorohydroquinone disulfonic acid are formed (19)); for use of boilg. conc. HCl (9), conc. HBr (9) (10) in AcOH (3), with conc. HI + red (18) or yellow (20) phosphorus, or

with KI or NaI in cold acetone (38) see indic. refs.; for use of H_2S (5), $SnCl_2$ + HCl (9) (8) (6), aq. slightly alkaline hydroxylamine (13), alc. hydrazine hydrate (21), with EtOH on exposure to direct sunlight (7) (study of quantum efficiency of the photochemical reduction (22)), or with hydroquinone (1:1590) in ether (39) see indic. refs.]

[For formn. of $\bar{C}$ as by-product of use of tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) in low-temp. dehydrogenations see (23) (24); for formn. of derivatives (ethers) of $\bar{C}$ as by-products of reaction of chloranil (3:4978) with free radicals see (25) (26) cf. (27); for formn. of $\bar{C}$ as by-product of reaction of chloranil (3:4978) with C_6H_5MgBr see (31).]

From 2,3,5-trichlorobenzoquinone-1,4. [For prepn. of $\bar{C}$ from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with conc. HCl on protracted boilg. (9) (28), with fumg. HCl in s.t. at 120° for 12 hrs. (29), or in AcOH soln. with dry HCl gas (30) see indic. refs.]

From other sources. [For formn. of $\bar{C}$ from hydroquinone (1:1590) in AcOH with Cl_2 (32), or from *p*-nitroaniline (or certain derivatives) with conc. HCl in s.t. at 180° (2), see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Oxidation of $\bar{C}$. $\bar{C}$ on oxidation, e g., with aq. alc. $AgNO_3$ (10), $NH_4OH/AgNO_3$ (2), boilg. conc. HNO_3 (2) (20), etc., gives tetrachlorobenzoquinone-1,4 (chloranil) (3:4978).

[For studies of oxidn.-reductn. potential of system $\bar{C}$ + chloranil see (33) (34) (35) (1) (27) (6).]

[Note also that the quinhydrone to be expected from $\bar{C}$ with 1 mole of the corresp. tetrachlorobenzoquinone-1,4 (chloranil) (3:4978) is not reported.]

[Note also that, although $\bar{C}$ dissolves in aq. KOH without discoloration, the soln. upon exposure to air turns brown and on stdg. ppts. (16) di-potassium salt of chloranilic acid (2,5-dichloro-3,6-dihydroxybenzoquinone-1,4) (3:4970).]

Other reactions of $\bar{C}$. [$\bar{C}$ with PCl_5 (2 moles) gives (16) hexachlorobenzene (3:4939).— $\bar{C}$ with 2,3,5-trichlorohydroquinone (3:4052) + a little aq. htd. at 100° for ½ hr. undergoes a redistribution reaction (28) cf. (36).]

- Ⓓ Tetrachlorohydroquinone dimethyl ether: m.p. 164° (37), 160° (5). [From $\bar{C}$ by action of diazomethane in ether soln. (5).]
- Ⓓ Tetrachlorohydroquinone diethyl ether: m.p. 112° (16). [From $\bar{C}$ with EtI (2 moles) + KOH (2 moles) in alc. in s.t. at 130–140° (16).]
- Ⓓ Tetrachlorohydroquinone diacetate: m.p. 245° (16), 244–246° (7). [From $\bar{C}$ with AcCl (3:7065) (16) or from chloranil (3:4978) with AcCl in s.t. at 160–180° (16).]
- Ⓓ Tetrachlorohydroquinone dibenzoate: m.p. 233° (9). [From $\bar{C}$ with BzCl (3:6240) (9).]

3:4941 (1) Hall, Conant, *J. Am. Chem. Soc.* **49**, 3050–3052 (1927). (2) König, *J. prakt. Chem.* (2) **70**, 32–35 (1904). (3) Koenigs, Greiner, *Ber.* **64**, 1047 (1931). (4) Sutkowski, *Ber.* **19**, 2316 (1886). (5) Binz, Räth, *Ber.* **58**, 312 (1925). (6) Conant, Fieser, *J. Am. Chem. Soc.* **45**, 2207–2219 (1923). (7) Klinger, *Ann.* **382**, 221 (1911). (8) Bouveault, *Ann. chim.* (8) **13**, 144 (1908). (9) Levy, Schultz, *Ann.* [illegible]

(11) A. S. Coolidge, [illegible]

Svensk Kem. Tid. **48**, 12 [illegible]

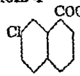
chim. (7) **21**, 501–507 [illegible]

(1925). (15) Fisher (to Naugatuck Chem. Co.), French 740,978, Feb. 3, 1933; *Cent.* **1933**, I 3134; *C.A.* **27**, 2845 (1933). (16) Graebe, *Ann.* **146**, 9–12, 18–21 (1868). (17) Bouveault, *Compt. rend.* **129**, 55 (1899). (18) Graebe, *Ann.* **263**, 28–30 (1891). (19) Dodgson, *J. Chem. Soc.* **1930**, 2501–2502. (20) Stenhouse, *Ann. Suppl.* **6**, 213–216 (1868).

(21) Purgotti, *Gazz. chim. ital.* **24**, I 581–584 (1894). (22) Leighton, Dresia, *J. Am. Chem. Soc.* **52**, 3556–3562 (1930). (23) Arnold, Collins, Zenk, *J. Am. Chem. Soc.* **62**, 983–984 (1940). (24) Arnold, Collins, *J. Am. Chem. Soc.* **61**, 1407–1408 (1939). (25) Ziegler, Orth, *Ber.* **65**, 628–631 (1932). (26) Clar, John, *Ber.* **63**, 2974–2977 (1930). (27) Conant, Small, Taylor,

J. Am. Chem. Soc. **47**, 1959–1974 (1925). (28) Graebe, *Ann.* **263**, 21–22 (1891). (29) Andresen, *J. prakt. Chem.* (2) **28**, 425– (1883). (30) Niemeyer, *Ann.* **228**, 324 (1885).
(31) Clar, Engler, *Ber.* **64**, 1600 (1931). (32) Eckert, Endler, *J. prakt. Chem.* (2) **104**, 82 (1922). (33) Wallenfels, Möhle, *Ber.* **76**, 927, 936 (1943) (34) Kvalnes, *J. Am. Chem. Soc.* **56**, 667–670 (1934). (35) Hunter, Kvalnes, *J. Am. Chem. Soc.* **54**, 2869–2881 (1932). (36) Kehrmann, *Ber.* **31**, 979 (1898); **33**, 3066–3067 (1900). (37) Ciamician, Silber, *Gazz. chim. ital.* **22**, II 60 (1892) (38) Torrey, Hunter, *J. Am. Chem. Soc* **34**, 714–715 (1912) (39) Siegmund, *J. prakt. Chem.* (2) **92**, 362 (1915) (40) Sarauw, *Ann.* **209**, 125 (1881)

3:4942 7-CHLORONAPHTHOIC ACID-1 $C_{11}H_7O_2Cl$ Beil. S.N. 951



M.P. 243° cor. (1)
238–240° (3)
235° (3)

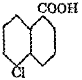
Cryst. from 60% alc. or by sublimation. — Very sol. alc. or AcOH; sol. ether, C_6H_6.

[For prepn. of C̄ from 7-aminonaphthoic acid-1 (1) (2) via diazotization and use of Cu_2Cl_2 reactn. see (1); from 7-chloro-1-(chloromethyl)naphthalene, m.p. 75° (3), by oxdn. with dil. HNO_3 see (3), from 7-chloro-1-bromonaphthalene [Beil. V-548] via conv. to RMgBr and carbonation see (3).]

C̄ with PCl_5 or $SOCl_2$ yields (1) 7-chloro-1-naphthoyl chloride, yel. cryst. from pet. eth., m.p. 106° cor (1).

- Ⓓ **Methyl 7-chloro-1-naphthoate:** cryst from 60% MeOH, m.p. 54° cor. (1). [From C̄ in MeOH with conc. H_2SO_4 (90% yield (1)).]
- —— **Ethyl 7-chloro-1-naphthoate:** unreported.
- Ⓓ ***p*-Bromophenacyl 7-chloro-1-naphthoate:** m.p. 145–146° (3).
- Ⓓ **7-Chloro-1-naphthoamide:** colorless ndls. from 50% alc., m.p. 237° cor. (1). [From the acid chloride (above) with 4 pts. conc. aq. NH_4OH at ord. temp. for 2 hrs. (75% yield (1)).]
- Ⓓ **7-Chloro-1-naphthoanilide:** brownish ndls. from dil. alc., m p. 185° cor. (1). [From *the acid chloride (above) with 5 pts. aniline at 100° (80% yield (1)).]*

3:4942 (1) Goldstein, Fischer, *Helv. Chim. Acta* **21**, 1519–1521 (1938). (2) Harrison, Royle, *J. Chem. Soc.* **1926**, 87. (3) Horn, Warren, *J. Chem. Soc.* **1946**, 144.

3:4944 5-CHLORONAPHTHOIC ACID-1  $C_{11}H_7O_2Cl$ Beil. IX-651
IX_1—

M.P. 245° (1)
244–245° (3)

Ndls. which sublime even below m.p. — Eas sol. alc, spar. sol. C_6H_6 or AcOH.

[For prepn. of C̄ from α-naphthoic acid (1:0785) with Cl_2 in AcOH contg. I_2 (some of the isomeric 8-chloronaphthoic acid-1 (3:4680) also being formed) see (1); from 5-chloro-1-naphthonitrile (see below) on hydrolysis with fumg. HCl in s.t. see (1); from 5-aminonaphthoic acid-1 [Beil. XIV-533] via diazotization and use of Cu_2Cl_2 reactn. see (1); for

formn. (together with other prods.) from α-naphthoic acid (1:0785) via reactn. with $Hg(OAc)_2$ followed by treat. with Cl_2 in AcOH see (3).]

Salts. $Ca\bar{A}_2.2H_2O$; sol. in 116 pts. aq. at ord. temp. (1).

$\bar{C}$ on soln. in red. fumg. HNO_3 gives (2) on cooling 5-chloro-8-nitronaphthoic acid-1 [Beil. IX-654], ndls. from alc., m.p. 224–225° dec. (2) (ethyl ester, m.p. 121° (2)); if the soln. of $\bar{C}$ in red fumg. HNO_3 be heated there is also formed (2) some 4-chloro-1,8-dinitronaphthalene [Beil. V-561], pale yel. ndls. from AcOH, m.p. 180° (3), 175° (2).

—— **Methyl 5-chloro-1-naphthoate:** unreported.

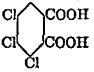
Ⓓ **Ethyl 5-chloro-1-naphthoate:** tbls. from alc., m.p. 42° (1). [From $Ag\bar{A}$ with EtI in s.t. at 100° (1).]

—— **5-Chloro-1-naphthonitrile:** ndls. from alc., m.p. 145° (1). [From α-naphthonitrile [Beil. IX-649, IX_1-(275)] with Cl_2 in CS_2 contg. I_2 (1).]

—— **5-Chloro-1-naphthoamide:** lfts. or ndls. from warm alc., m.p. 239° (1). [From 5-chloro-1-naphthonitrile (above) on boilg. with alc. KOH for several hrs. (1).]

3:4944 (1) Ekstrand, *J. prakt. Chem.* (2) 38, 147–150 (1888). (2) Ref. 1, pp 170–171. (3) Atterburg, *Ber.* 9, 928 (1876). (3) Whitmore, Fox, *J. Am. Chem. Soc.* 51, 3366–3367 (1929).

3:4946 TETRACHLOROPHTHALIC ACID



$C_8H_2O_4Cl_4$ Beil. IX - 819 IX_1-(366)

M.P. See text.

[*See also tetrachlorophthalic anhydride* (3:4947).]

Colorless lfts., tbls., or ndls. from aq. invariably contg. ½ H_2O, and therefore giving in this form Neut. Eq. = 156.5. — This hemihydrate can be recrystd. from anhyd. ether without change. — From anhyd. acetone the acid separates in cryst. contg. combined solv. lost in stream of dry air at room temp., yielding anhyd. $\bar{C}$, Neut. Eq. 152, which absorbs aq. from air giving hemihydrate. — $\bar{C}$ on htg. at 98° or above, or on attempts to recryst. from dry C_6H_6, $CHCl_3$, or higher-boilg. solvents, or on long drying over P_2O_5 in vac., is converted to tetrachlorophthalic anhydride (3:4947); for this reason the m.p. observed for $\bar{C}$ is always actually that of the corresponding anhydride. — For purification of comml. $\bar{C}$ see (1) (13).

$\bar{C}$ is spar. sol. aq., e.g., 100 g. aq. at 14° dis. 0.57 g., at 99° 3.03 g. of hemihydrate (2); $\bar{C}$ is eas. sol. alc. or ether (2); extremely sol. in acetone (1); spar. sol. C_6H_6 or $CHCl_3$ (2). — $\bar{C}$ is sol. in hot aq. Na_2CO_3 soln. (dif. from tetrachlorophthalic anhydride (3:4947)).

[For prepn. of $\bar{C}$ via hydrolysis of tetrachlorophthalic anhydride (3:4947) see that cpd.; other methods include the following: from phthalic anhydride (1:0725) (3), from phthalyl dichloride (3:6900) (4), or phthalic acid (1:0820) (5) with Cl_2 in pres. of Fe or $FeCl_3$ see indic. refs.; from 2-(trichloroacetyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X-693], with dil. aq. NaOH see (6); from 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X_1-358], with conc. H_2SO_4 at 200–250° (pentachlorobenzene (3:2290) is also formed) see (7); from naphthoquinone-1,2 (1:9062), anthraquinone (1:9095), 1,2,3,4,5,6,7-heptachloroanthraquinone [Beil. VII_1-(414)], or 2-(pentachlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid (see above) on boilg. with excess $SbCl_5$ + a little I_2 see (7) (8); from 1,2,3,4,5-pentachloronaphthalene [Beil. V-546] (9) (10), 1,2,3,4,5,6,8-heptachloronaphthalene [Beil. V-547] (11), or octachloronaphthalene (3:4893) (12) by oxidn. with HNO_3 in s.t. as directed

see indic. refs.; from 2,5,6,7,8-pentachloronaphthoquinone-1,4 [Beil. VII-731] by oxidn. with CrO_3 or HNO_3 see (11).]

[$\bar{C}$ with Na/Hg in dil. aq. alc. (10) (2) yields phthalic acid (1:0825), but $\bar{C}$ in 96% alc. with Na/Hg is practically unaffected (1) (2). — $\bar{C}$ with H_2 in pres. of finely divided Ni at 190° and 20 atm. press. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p. 208.5° cor. — $\bar{C}$ with HI + P in s.t. at 230° for 6 hrs. yields (2) 4,5,6,7-tetrachlorophthalane [Beil. XVII-51], ndls. from toluene, m.p. 218° (2) (insol. in boilg. aq. NaOH), accompanied by a little 4,5,6,7-tetrachlorophthalide (above) (sol. in boilg. aq. NaOH).]

$\bar{C}$ with CrO_3 oxidizes much more slowly (2) than phthalic acid (1:0825) and is very resistant toward HNO_3 (2); for detn. of chlorine in $\bar{C}$ see (1) (16)

[$\bar{C}$ with aq. KOH + KCN + CuCN htd. under press. at 180° for 8–10 hrs. gives (60% yield (15)) benzenehexacarboxylic acid (mellitic acid) [Beil. IX-1008, IX_1-(443)]. — $\bar{C}$ with HBr + H_3PO_4 in nitrobenzene in pres. of $CuCl_2$ yields (17) mixts. of bromotrichlorophthalic acids and dibromodichlorophthalic acids. — For actn. of PCl_5 see under tetrachlorophthalic anhydride (3:4947). — $\bar{C}$ with hydrazine hydrate at 150° gives only (18) *N*-aminotetrachlorophthalimide, colorless ndls. from AcOH, m.p. 288° dec. (18); earlier opinions (19) (20) that this prod. was tetrachlorophthalcyclohydrazide have been shown (18) to be erroneous. — $\bar{C}$ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (21) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p. 186°.]

[For use of $\bar{C}$ as softener for animal fibers see (22) (23). — For use of $\bar{C}$ in prepn. of α-borneol (1·5990) from turpentine oil (crude pinene) by htg. at 108° for 12 hrs., removal of unchanged terpenes by distn. and alc. NaOH saponification of the remaining di-bornyl tetrachlorophthalate, white cryst. from ether, m.p. 128–129° (24), see (24) (25).]

Salts. $K_2\bar{A}$, very sol. aq., spar. sol. alc. (2), $Ba\bar{A}.2\frac{1}{2}H_2O$ see (2); $Ca\bar{A}$, on htg. gives octachloroanthraquinone [Beil VII-789] (17); $Cu\bar{A}.2H_2O$, spar. sol. aq. (2) (earlier report (27) that on dry distn. it gives dodecachlorofluorane later seriously questioned (28)); $Zn\bar{A}$, very sol. aq. (more sol. cold aq. than hot aq.) (2); $Ag_2\bar{A}$, spar. sol. aq.

Ⓓ **Dimethyl tetrachlorophthalate:** cryst. from MeOH, m.p. 92° (2). [From $Ag_2\bar{A}$ with MeI (2), from *sym*-tetrachlorophthalyl (di)chloride with NaOMe (2) or from $\bar{C}$ in 10% aq. NaOH (3 moles) on warming with Me_2SO_4 (29); note that $\bar{C}$ in MeOH satd. with HCl gas gives (30) only the half ester, methyl hydrogen tetrachlorophthalate, cryst. from C_6H_6 on addn. of lgr., m.p. 142° (30) with elimination of MeOH and conversion to tetrachlorophthalic anhydride (3:4947) q.v.]

Ⓓ **Diethyl tetrachlorophthalate:** cryst., m.p. 60–60.5° (2) (31). [From $Ag_2\bar{A}$ + EtI (2) or from *sym.*-tetrachlorophthalyl (di)chloride + NaOEt (2); note that *unsym.*-tetrachlorophthalyl (di)chloride with abs. alc at room temp. gives (31) *pseudo*-diethyl tetrachlorophthalate, tbls. from alc., m.p. 126° (19), and that this cpd. on stdg. in the reactn. mixt. is partially conv. to the normal ester of m p. 60.5° (31).]

Ⓓ **Di-(*p*-nitrobenzyl) tetrachlorophthalate:** ndls. from C_6H_6, or from aq. alc., m.p. 180–181° (32), 179–180° (33) [From $Na_2\bar{A}$ + *p*-nitrobenzyl bromide on refluxing in alc. (32), or from $Ag_2\bar{A}$ + *p*-nitrobenzyl iodide (33).]

Ⓓ **Di-(*p*-phenylphenacyl) tetrachlorophthalate:** cryst. from acetone, m.p. 193° (34). [From $Na_2\bar{A}$ with *p*-phenylphenacyl bromide (2 moles) on htg. in alc. (34).]

3:4946 (1) Delbridge, *Am. Chem. J.* **41**, 393–415 (1909). (2) Graebe, *Ann.* **238**, 318–332 (1887). (3) Zal'kind, Belikova, Simonova, Russ 39,761, Nov. 30, 1934; *Cent.* **1935**, II 3441; *C.A.* **30**, 3443 (1936); Russ. 46,568, April 30, 1936; *Cent.* **1936**, II 2798. (4) Zal'kind, Belikova, Russ. 35,183, March 31, 193[illegible]

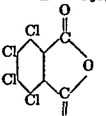
Cent. **1936**, II 2798. [illegible]

Cent **1930**, II 3414; [illegible]

Eckert, Steiner, *Mona* [illegible]

36, 827 (1915). (9) Graebe, *Ann.* **149**, 18–20 (1869). (10) Claus, Spruck, *Ber.* **15**, 1402–1403 (1882).
(11) Claus, Wenzlik. *Ber.* **19**, 1166–1167 (1886). (12) Shvemberger, Gordon, *J. Gen. Chem.* (*U.S.*
4, 695
Soc. **4**
Feist, *Ber.* **68**, 1941–1943 (1935). (16) Heslinga, *Rec. trav. chim.* **43**, 182 (1924). (17) Brück (to I.G.), Ger. 597,259, May 25, 1934; *Cent.* **1934**, 1688. (18) Drew, Pearman, *J. Chem. Soc.* **1937**, 27, 32–33. (19) Phelps, *Am. Chem. J.* **33**, 586 (1905). (20) Radulescu, Alexa, *Bul. Soc. Chim. România* **12**, 163 (1930); *C.A.* **25**, 4001 (1931).
(21) Jaeger (to Selden Co.), U.S. 1,964,516, June 26, 1934; *Cent.* **1934**, II 3047. (22) Schwen, Krzikalla (to I.G.), U.S. 1,887,958, Nov. 15, 1932; French 704,423, May 20, 1931; *Cent.* **1931**, II 3286. (23) Dreyfus, French 749,792, July 29, 1933; *Cent.* **1934**, I 3154. (24) Haller, *Compt. rend.* **178**, 1933–1937 (1924); *Cent.* **1924**, II 642. (25) Haller, U.S. 1,415,340, May 9, 1922; *Cent.* **1923**, IV 946; *C.A.* **16**, 2335 (1922); Brit. 158,533, March 3, 1921; *Cent.* **1921**, IV 422. (26) Kircher, *Ber.* **17**, 1170 (1884). (27) Ekely, Mattison, *J. Am. Chem. Soc.* **52**, 3003–3004 (1930). (28) Ekely, *J. Am. Chem. Soc.* **54**, 406 (1932). (29) Graebe, *Ann.* **240**, 247 (1905). (30) Meyer, Sudborough, *Ber.* **27**, 3148–3149 (1894).
(31) Kirpal, Junze, *Ber.* **62**, 2105 (1929). (32) Lyons, Reid, *J. Am. Chem. Soc.* **39**, 1741, 1744 (1917). (33) Meyer, Jugilewitsch, *Ber.* **30**, 785–786 (1897). (34) Drake, Sweeney, *J. Am. Chem. Soc.* **54**, 2059–2061 (1932).

3:4947 TETRACHLOROPHTHALIC ANHYDRIDE $C_8O_3Cl_4$ Beil. XVII - 484 XVII$_1$-(254)



M.P.	255–257° cor.	(1)
	255–256.5° cor.	(2)
	255°	(3)
	252° (4), cor.	(5)
	245° u.c.	(5)

[*See also tetrachlorophthalic acid* (3:4946).]

Colorless pr. or ndls. by sublimation. — Insol. cold aq., but sol. in boilg. aq. because of hydrolysis to tetrachlorophthalic acid (3:4946); spar. sol. ether. — C̄ is insol. in Na_2CO_3 soln. (dif. from tetrachlorophthalic acid (3:4946)).

[For prepn. of C̄ from tetrachlorophthalic acid (3:4946) by htg. above m.p. (6), by htg. 8 hrs. at 110° (7), by htg. 120 hrs. at 100° (8) (9), by sublimation, htg. at 98°, by crystn. from hot C_6H_6, $CHCl_3$, AcOH (2), or by protracted drying over P_2O_5 in vac. (1) cf. (5) (10) see indic. refs.; from phthalic anhydride (1:0725) with Cl_2 in pres. of Fe salts at 160–260° (11), or with Cl_2 in pres. of $SbCl_5$ at 200° (10) (12), or with Cl_2 in pres. of fumg. H_2SO_4 (50–60% SO_3) and I_2 (2) (13) see indic. refs.; from naphthalene (1:7200) with $ClSO_3H$ in s.t. at 180° see (3).]

[C̄ on reduction with Zn dust + hot AcOH (10) or with H_2 + Ni at 190° and 20 atm. yields (14) 4,5,6,7-tetrachlorophthalide [Beil. XVII-312], m.p. 208.5° cor.]

C̄ reacts with monohydric alcs. to yield corresp. half esters: e.g., C̄ dislvd. in excess warm MeOH, htd. 5–10 min., evapd. yields (15) methyl hydrogen tetrachlorophthalate [Beil. IX-820], cryst. from hot C_6H_6 on addn. of lgr., m.p. 139–140° (15), 142° (16), Neut. Eq. 318; C̄ with abs. EtOH treated as for preceding case gives (15) ethyl hydrogen tetrachlorophthalate, m.p. 93–94° (15), 94–95° (10), Neut. Eq. 332. — [C̄ with *ter*-butyloxymagnesium

bromide in ether + dioxane at 50-55° for 1 hr. gives (54% yield (17)) *ter*-butyl hydrogen tetrachlorophthalate, decomposing at 142°, Neut. Eq. 360; for analogous formn. of *ter*-amyl, triethylcarbinyl, tri-*n*-propylcarbinyl, tri-*n*-butylcarbinyl and tri-*n*-amylcarbinyl hydrogen tetrachlorophthalates see (17).] — [For reactn. of $\bar{C}$ with glycerol and use in prepn. of resins of glyptal type see (3) (18).]

[$\bar{C}$ with 1 mole PCl_5 in s.t. 4 hrs. at 220° (19) cf. (10) or $\bar{C}$ with 1 mole PCl_5 + $POCl_3$ refluxed 72 hrs. (20) gives (90% yield (20)) *unsym.*-tetrachlorophthalyl (di)chloride (3,3,4,5,6,7-hexachlorophthalide) [Beil. XVII$_1$-(484)], cryst. from C_6H_6 with 1 mole solvent, m.p. 118° (10) (20), 118–120° (19), but losing C_6H_6 in air to give solvent free cpd., ndls. from pet. ether, m.p. 137° (19) (20); this prod. on distn. (19) undergoes partial rearr. to *sym.*-tetrachlorophthalyl (di)chloride, pr. from pet. ether, m.p. 48° (19). — Note that the latter *sym.*-phthalyl (di)chloride (which is very soluble in most org. solvents) gradually changes even in solid form and very rapidly in solution (particularly in pres. of animal charcoal) to the *unsym.*-tetrachlorophthalyl (di)chloride (which is spar. sol. in most org. solvents) (19). — $\bar{C}$ with $SOCl_2$ + $ZnCl_2$ at 200–240° yields (21) cf. (22) tetrachlorophthalyl (di)chloride but whether the *unsym.* or *sym.* forms or their mixture is not stated. — Note also that with abs. EtOH the *unsym.* acid chloride yields (19) *pseudo* diethyl tetrachlorophthalate, tbls. from alc., m.p. 126° (19), while the *sym.* acid chloride gives (19) *sym.* diethyl tetrachlorophthalate, m.p. 60.5° (19).]

[$\bar{C}$ with 2 moles PCl_5 in s.t. at 200° for 5–6 hrs. yields (10) a prod. (regarded as either 1,1,3,3,4,5,6,7-octachlorophthalide or 2-(trichloromethyl)-3,4,5,6-tetrachlorobenzoyl chloride), cryst. from ether, m.p. 140° (10), and practically unaffected by warm alc. KOH.]

[$\bar{C}$ with arom. hydrocarbons + $AlCl_3$ yields corresp. *o*-aroyl-tetrachlorobenzoic acids: e.g., $\bar{C}$ with C_6H_6 + $AlCl_3$ (23) (24) (25) or $\bar{C}$ with C_6H_5MgBr (26) gives 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid [Beil. X-750], ndls. from 80% AcOH or C_6H_6, m.p. 201° (24), 200° (23), 188–189° (26), which on ring closure with 20 pts. conc. H_2SO_4 at 200° for 5 min. (23) gives 1,2,3,4-tetrachloroanthraquinone [Beil. VII-789], gold-yel. lfts., m.p. 191° (23). — $\bar{C}$ with toluene + $AlCl_3$ gives (yields: 100% (27), 95% (28), 94% (29)) 2-(*p*-toluyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from C_6H_6, m.p. 174.5° cor. (29), 172° (28) (30) (the value of 142° (27) may be a misprint for 172°), which on ring closure with 12 pts. $H_2SO_4.H_2O$ at 190–200° for 2 min. (27) or with 9 pts. fumg. H_2SO_4 (2% SO_3) at 120–130° for 30 min. (28) gives (21% yield (28)) 2-methyl-5,6,7,8-tetrachloroanthraquinone, yel. ndls from toluene, m.p. 195–196° (27), or from EtOAc, m.p. 192° (28) — For corresp. reactns. of $\bar{C}$ with *o*-xylene (1:7430), *m*-xylene (1:7420), *p*-xylene (1:7415), and ethylbenzene (1:7410) and use in identif. of these cpds. see (7). — For reactn. of $\bar{C}$ with α-naphthyl MgBr, *p*-methoxyphenyl MgBr, or *p*-bromphenyl MgBr yielding corresp. *o*-aroyl-tetrachlorobenzoic acids see (26).]

[$\bar{C}$ with chlorobenzene (3:7903) + $AlCl_3$ at 140° for 3 hrs. gives (92% yield (31)) 2-(*p*-chlorobenzoyl)-3,4,5,6-tetrachlorobenzoic acid, cryst. from AcOH, m.p. 162–165° (31), which with conc H_2SO_4 at 140° for 30 min. gives 2,5,6,7,8-pentachloroanthraquinone, yel. cryst. from AcOH, m.p. 192° (31). — For corresp. reactns. of $\bar{C}$ with *p*-dichlorobenzene (3:0980), with 1,2,4-trichlorobenzene (3:6120), or with nitrobenzene see (31).]

[$\bar{C}$ with phenols and appropriate condensing agents gives two different types of reactns. according to circumstances, viz., formation of corresp. *o*-hydroxyaroyltetrachlorobenzoic acids (cf. above) or of corresp. tetrachlorophthaleins. — E.g., $\bar{C}$ with 1 mole phenol + $AlCl_3$ in acetylene tetrachloride at 125° for 3 hrs gives (yields: 79% (32), 82% (33)) 2-(o-hydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid [Beil. X$_1$-(470)], lfts. from xylene/AcOH, m.p. 216–218° cor. (32), 210° (33), which with boilg. NaOH loses HCl and ring-closes to 2,3,4-trichloroxanthonecarboxylic acid-1 [Beil. XVIII$_1$-(499)], colorless ndls. from alc., m.p. 261–264° cor. (32), 262–265° dec. (33). — For corresp. reactns. of $\bar{C}$ with

o-cresol (1:1400) (32) (34), *m*-cresol (1:1730) (32), *p*-cresol (1:1410) (32), α-naphthol (1:1500) (38), β-naphthol (1:1540) (32), anisole (1:7445) (34) see indic. refs., with hydroquinone (1:1590) + $AlCl_3$ + NaCl at 150–155° for 1½ hrs. giving 82% yield 2-(2′,5′-dihydroxybenzoyl)-3,4,5,6-tetrachlorobenzoic acid, m.p. 231°, or on further htg. in the above melt at 210–215° for 1 hr. ring closing to 1,4-dihydroxy-5,6,7,8-tetrachloroanthraquinone, red cryst. from xylene, m.p. 247°, see (35). — However, C̄ with 2 moles phenol in pres. of fumg. H_2SO_4 (20% SO_3) as directed (8) (36) gives 65% yield phenoltetrachlorophthalein [Beil. XVIII-148, $XVIII_1$-(375)], m.p. 316–317° dec. (36), accompanied by about 10% (37) of 3′,4′,5′,6′-tetrachlorofluoran [Beil. XIX-148, XIX_1-(676)], colorless pr. from C_6H_6, m.p. 298° dec. (33), 290–291° (37) (for sepn. of this by-prod. from the phenoltetrachlorophthalein see (37)). — For condens. of C̄ with *o*-cresol (1:1400) to *o*-cresoltetrachlorophthalein see (45); with resorcinol (1:1530) to 3′,4′,5′,6′-tetrachlorofluorescein [Beil. XIX-227, XIX_1-(722)] see (10) (9).]

[For condens. of C̄ with *m*-diethylaminophenol see (39); with *N*-aryl-*m*-aminophenols in prepn. of phthalein dyes see (40); for condens. of C̄ with hydroxyisodibenzanthrone in prepn. of vat dyes see (41); for use of C̄ as textile softener see (42).]

[C̄ with steam passed over cat. at 380–420° loses CO_2 presumably yielding (43) 2,3,4,5-tetrachlorobenzoic acid [Beil. IX-346], m.p. 186°.]

C̄ on fusion and treatment with NH_3 gas (10) (4), or on warming with formamide (2), or on fusion with $(NH_4)_2CO_3$ (47) gives (yields: 91% (2), 90% (47)) tetrachlorophthalimide [Beil. XXI-505, XXI_1-(391)], lfts. from AcOH, dimethylaniline or nitrobenzene, m.p 338–339° cor. (2), 336–337° (47); for reactn. of this prod. with KOMe forming K tetrachlorophthalimide and use of latter in identification of alkyl halides, etc., see (47). — [For reactn. of C̄ with hydrazine hydrate in dil. alc. yielding *N*-aminotetrachlorophthalimide, ndls. from AcOH, m.p. 288° dec., see (48); for reactn. of C̄ with hydroxylamine in aq. and in MeOH see (49). — C̄ in boilg. AcOH treated with aniline yields (2) cf. (50) *N*-phenyltetrachlorophthalimide (tetrachlorophthalanil) [Beil. XXI-505, XXI_1-(391)], m.p. 274–275° cor. (2). — For reactn. of C̄ with *o*-phenylenediamine see (6).]

C̄ on warming with aq., or with aq. alk. followed by acidification, yields tetrachlorophthalic acid (3:4946) q.v. [For use of differential hydrolysis of C̄ in sepn. from 3,4-dichlorophthalic anhydride (3:3695), 3,6-dichlorophthalic anhydride (3:4860), or 4,5-dichlorophthalic anhydride (3:4830) see under these cpds.]

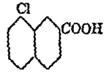
3:4947 (1) Delbridge, *Am. Chem. J.* **41**, 400, 402, 406, 408–409, 415–416 (1909). (2) Pratt, Perkins, *J. Am. Chem. Soc.* **40**, 204–214 (1918). (3) Walter, *Monatsh.* **64**, 287–288 (1934). (4) Pfeiffer, *Ber.* **55**, 421–425 (1922). (5) Graebe, *Ann.* **149**, 18–20 (1869). (6) Bistrzycki, Lecco, *Helv. Chim. Acta* **4**, 430–431 (1921). (7) Underwood, Walsh, *J. Am. Chem. Soc.* **57**, 941 (1935). (8) Orndorff, Black, *Am. Chem. J.* **41**, 359–393 (1909). (9) Orndorff, Adamson, *J. Am. Chem. Soc.* **40**, 1239–1257 (1918). (10) Graebe, *Ann.* **238**, 318–338 (1887).

(11) Dvornikoff (to Monsanto Chem. Co.), U.S. 2,028,383, Jan. 21, 1936; *Cent.* **1936**, I 2830; *C.A.* **30**, 1394 (1[illegible] *Fried-länder*, **1**, 318. [illegible] , 5, 1923; *Cent.* **192**[illegible] [illegible]or-ough, *Ber.* **27**, [illegible] [illegible]6).
(18) Kogan, Ponomarenko, *Org. Chem. Ind.* (*U.S.S.R.*) **7**, 382–385 (1940); *C.A.* **35**, 4118 (1941). (19) Kirpal, Kunze, *Ber.* **62**, 2102–2106 (1929). (20) Kaufmann, Voss, *Ber.* **56**, 2511–2512 (1923).

(21) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,364, March 20, 1934; *Cent* **1934**, II 333. (22) Kyrides, *J. Am. Chem. Soc.* **59**, 206–208 (1937). (23) Kircher, *Ann.* **238**, 338–346 (1887). (24) Meyer, *Monatsh.* **25**, 1189–1191 (1904). (25) Müller (to I.G.), Ger. 495,447, April 7, 1930; *Cent.* **1931**, I 1675. (26) C. Weizmann, E. Bergmann, F. Bergmann, *J. Chem. Soc.* **1935**, 1367–1369. (27) Eckert, Endler, *J. prakt. Chem.* (2) **102**, 335–336 (1921). (28) Ruggli, Brunner, *Helv. Chim. Acta* **8**, 160–161 (1925). (29) Lawrance, *J. Am. Chem. Soc.* **43**, 2580 (1921). (30) M.L.B., French 520,542, June 27, 1921; *Cent.* **1921**, IV 804: Brit. 160,433, April 14, 1921; *Cent.*

1921, IV 127: Swiss 89,059, Aug. 1, 1921; *Cent.* 1922, II 145: Ger. 360,422, Oct. 2, 1922; *Cent.* 1923, II 190.
(31) Hofmann, *Monatsh* 36, 812–818 (1915). (32) Ullmann, Schmidt, *Ber.* 52, 2113–2118 (1919). [illegible] 48, 283–285 (1926). (34) Orndorff, Murray, *J. Am.* [illegible] ldmann, *J. prakt. Chem.* (2) 147, 333 (1936/1937). [illegible] oc. 38, 2487 (1916). (37) Orndorff, Kennedy, *J. Am.* [illegible] op, Norris, Weizmann, *J. Chem. Soc.* 95, 286

3:4948 8-CHLORONAPHTHOIC ACID-2 $C_{11}H_7O_2Cl$ Beil. IX - 662
IX_1—



M.P. 260° (1)

Fine ndls. best purified by sublimation (1)

[For prepn. of $\bar{C}$ from 8-aminonaphthoic acid-2 [Beil. XIV-536] via diazotization and use of Cu_2Cl_2 reactn. see (1).]

Salts. (1). $Ca\bar{A}_2.7H_2O$; $Ba\bar{A}_2.6H_2O$; both spar. sol. cold aq. but eas sol. hot aq.

$\bar{C}$ with Cl_2 in AcOH contg. I_2 yields (1) 5,8-dichloronaphthoic acid-2 [Beil. IX-662], ndls. from alc., m.p. 287° (1) (ethyl ester, m.p. 64–65° (1)).

—— Methyl 8-chloro-2-naphthoate: unreported.

Ⓓ Ethyl 8-chloro-2-naphthoate: lfts. from alc., m.p. about 29° (1). [From $\bar{C}$ in EtOH with dry HCl gas (1).]

3:4948 (1) Ekstrand, *J. prakt. Chem.* (2) 43, 417–418, 421 (1891).

3:4950 3,5-DICHLORO-4-HYDROXYBENZOIC ACID $C_7H_4O_3Cl_2$ Beil. X - 176
X_1-(78)

M.P. 268–269° cor.	(1)
265° cor.	(2)
265°	(3)
259–260°	(4)
257–258.5°	(5)
255–256°	(6) (9)

White ndls. from dil. alc. or dil. AcOH; spar. sol. cold but more sol. hot aq; eas. sol. alc., ether; sublimes at 250–260° (7) without appreciable decompn. (6).

[For prepn. of $\bar{C}$ from *p*-hydroxybenzoic acid (1:0840) in 10% AcOH (1) or in aq. KOH (3 moles) (7) with Cl_2, or on htg. with $SbCl_5$ (4 moles) (6) or with 30% H_2O_2 + HCl as directed (80% yield (8)) see indic. refs.; from 3-sulfo-4-hydroxybenzoic acid in aq. with

Cl_2 see (9); from potassium 2,6-dichlorophenolate with CO_2 at 140° see (7); from ethyl 3,5-dichloro-4-hydroxybenzoate (see below) by hydrolysis with 35% aq. KOH (5) or with Claisen's alk. (95% yield (1)) see indic. refs.; from 3,5-dichloro-4-methoxybenzoic acid with 45% HI for 15 hrs. in s.t. at 130–140° see (3) (2).]

$\bar{C}$ on htg with CaO (4) (7), or with dimethylaniline at 190° (78% yield (1)), or with quinoline at 190–200°·(80–85% yield (10)) loses CO_2 giving 2,6-dichlorophenol (3:1595).

$\bar{C}$ in conc. aq. soln. gives with $FeCl_3$ a brown ppt. (4).

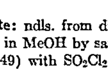
[$\bar{C}$ on electrolytic reduction in aq./alc./H_2SO_4 gives (11) 3,5-dichloro-4-hydroxybenzyl ethyl ether [Beil. VI-898], m.p. 86° (11); for prepn. and study of thermal rearr. of the crotyl ether of $\bar{C}$ see (1).]

Ⓓ **Methyl 3,5-dichloro-4-hydroxybenzoate:** ndls. from dil. alc. or lgr., m.p. 124° (3), 122° (12), 121–122° (4) (5). [From $\bar{C}$ in MeOH by satn. with HCl gas (3) (4); also from methyl *p*-hydroxybenzoate (1:1549) with SO_2Cl_2 (2 moles) (5).] [This prod. with acetyl chloride yields (5) corresp. acetate, lfts. from MeOH, m.p. 70–71° (5), 68–69° (4).]

Ⓓ **Ethyl 3,5-dichloro-4-hydroxybenzoate:** ndls. of monohydrate, m p. 108–116° cor. (1), 116° (5) from 80% alc.; after long drying in vac. over P_2O_5 lose aq. yielding anhydrous ester, m.p. 111–112° cor. (1); note that this ester is extracted from ether soln. by aq. $NaHCO_3$ and is also titratable with stand. alk. (Neut. Eq. of monohydrate 253). [From ethyl *p*-hydroxybenzoate (1:1534) with excess SO_2Cl_2 (5) in 85% yield (1).]

3:4950 (1) Tarbell, Wilson, *J. Am. Chem. Soc.* **64**, 1066–1070 (1942). (2) Durrans, *J. Chem. Soc.* **123**, 1426 (1923). (3) Bertozzi, *Gazz. chim. ital.* **29**, II 39 (1899). (4) Zincke, *Ann.* **261**, 250–252 (1891). (5) Mazzara, *Gazz. chim. ital.* **29**, I 387–388 (1899). (6) Lössner, *J. prakt. Chem.* (2) **13**, 434 (1876). (7) Tarugi, *Gazz. chim. ital.* **30**, II 490–491 (1900). (8) Leulier, Pinet, *Bull. soc. chim.* (4) **41**, 1365–1366 (1927). (9) Datta, Mitter, *J. Am. Chem. Soc.* **41**, 2038 (1919) (10) Blicke, Smith, Powers, *J. Am. Chem. Soc.* **54**, 1468 (1932).
(11) Mettler, *Ber.* **39**, 2940 (1906). (12) von Auwers, Reis, *Ber.* **29**, 2359 (1896).

3:4952 5-CHLORONAPHTHOIC ACID-2 $C_{11}H_7O_2Cl$ Beil. IX - 662 IX_1—



M.P. 270° cor. (1)
263° (2)

Ndls. from alc. or AcOH. — Sol. in hot alc., in C_6H_6 or AcOH. — Sublimes in ndls. even below m.p.

[For prepn. of $\bar{C}$ from 5-amino-2-naphthoic acid [Beil. XIV-536] via diazotization and use of Cu_2Cl_2 reactn. see (2); from 5-chloro-2-naphthonitrile (below) by hydrolysis in AcOH/H_2SO_4/aq. medium (alm. 100% yield (1)) or with alc. KOH (2) see indic. refs.]

$\bar{C}$ with PCl_5 yields (1) 5-chloro-2-naphthoyl chloride, m.p. 89° cor., sol. in pet. eth. or C_6H_6, but only very slowly hydrolyzed by aq. even on htg. (1).

$\bar{C}$ on mononitration by soln. in excess conc. HNO_3 ($D = 1.42$) yields (2) on cooling 5-chloro-*x*-nitronaphthoic acid-2, ndls. from AcOH, m.p. 271° (ethyl ester, m.p. 118°); $\bar{C}$ on dinitration with red fumg. HNO_3 + a little conc. H_2SO_4 yields (1) 5-chloro-*x,y*-dinitronaphthoic acid-2, ndls. from AcOH, m.p. about 243° (ethyl ester, m.p. 132°); $\bar{C}$ on trinitration by conversion to mononitro-$\bar{C}$ (above) and treatment with excess fumg. HNO_3 + conc. H_2SO_4 yields (1) 5-chloro-*x,y,z*-trinitronaphthoic acid-2, yel. cryst. from AcOH, m.p. 260–261° dec. (ethyl ester, m.p. 188°).

Salts (2) $Na\bar{A}.2H_2O$ sol. aq.; $Ca\bar{A}_2.3\frac{1}{2}H_2O$, sol. in 4430 pts. cold aq.; $Ba\bar{A}_2.4\frac{1}{2}H_2O$, very spar. sol. cold aq.

Ⓓ Methyl 5-chloro-2-naphthoate: m p. 81° cor. (1). [From $\bar{C}$ in MeOH with conc. H_2SO_4 (90% yield (1)).]

Ⓓ Ethyl 5-chloro-2-naphthoate: ndls. from alc., m p. 45° (2).

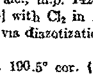
—— 5-Chloro-2-naphthonitrile: ndls. from alc., m.p. 142° cor. (1), 144° (2). [From 2-naphthonitrile [Beil IX-659, IX_1-(277)] with Cl_2 in AcOH contg. I_2 (2) or from 5-amino-2-naphthonitrile [Beil. XIV-536] via diazotization and use of Cu_2Cl_2 reactn. (28% yield (1)).]

—— 5-Chloro-2-naphthoamide: ndls, m.p. 190.5° cor. (1), 186–187° (2). [From 5-chloro-2-naphthonitrile (above) by hydrol. with alc. KOH (1) (2) or from acid chloride (above) with 4 pts. conc. aq NH_4OH for 2 hrs at ord. temp. (80% yield (1)).]

Ⓓ 5-Chloro-2-naphthoanilide: m.p 202.5° cor (1). [From the acid chloride (above) with 3 pts. aniline at 100° (90% yield (1))]

3:4952 (1) Goldstein, Matthey, *Helv Chim Acta* **21**, 65–66 (1938). (2) Ekstrand, *J. prakt. Chem* (2) **43**, 411–417 (1891).

3:4960 5-CHLOROISOPHTHALIC ACID (5-Chlorobenzenedicarboxylic acid-1,3) $C_8H_5O_4Cl$ Beil. IX - 838 IX_1—



M.P. 278° (1)

$\bar{C}$ cryst. from aq. in ndls. which even after drying over conc. H_2SO_4 cont. ½ mole H_2O; this water is lost, however, on htg. at 120° (1). — $\bar{C}$ is sol. at 15° in 3450 pts. aq. (1).

[For prepn. of $\bar{C}$ from 5-aminobenzenedicarboxylic acid-1,3 (5-aminoisophthalic acid) [Beil XIV-556, XIV_1-(636)] via diazotization and htg. sepg. diazonium salt with strong HCl see (1); from 5-chloro-3-methylbenzoic acid (3:4715) by oxidn. with $KMnO_4$ in dil. aq. KOH see (2).]

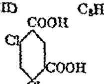
Salts. $Na_2\bar{A}$, $K_2\bar{A}$, eas. sol. aq. or alc.; $Ag_2\bar{A}$, ndls from aq.; $Mg\bar{A}$, $7H_2O$; $Ca\bar{A}$, $2H_2O$, sol. at 15° in 28 pts. aq.; $Sr\bar{A}$, H_2O, sol. at 15° in 108 pts. aq.; $Ba\bar{A}$, $2H_2O$ sol. at 15° in 71 pts. aq.; $Cd\bar{A}$, sol. at 15° in 330 pts. aq. (for details see (1)).

—— *Dimethyl 5-chloroisophthalate:* unrecorded.

Ⓓ Diethyl 5-chloroisophthalate: pr. from alc., m.p. 45° (1). [From $\bar{C}$ in EtOH with HCl gas (1).]

3:4960 (1) Beyer, *J. prakt. Chem.* (2) **25**, 506–515 (1882) (2) Klages, Knoevenagel, *Ber.* **28**, 2045–2046 (1895).

3:4965 4,6-DICHLOROISOPHTHALIC ACID (4,6-Dichlorobenzenedicarboxylic acid-1,3) $C_8H_4O_4Cl_2$ Beil. IX - 838 IX_1—



M.P. 279–281° (1)
280° u.c. (2)

Colorless ndls. from hot aq or dil. alc.; eas. sol. alc., ether, $CHCl_3$; insol. cold aq.

[For prepn. of $\bar{C}$ from 4,6-dichloro-1,3-dimethylbenzene [Beil. V-373, V_1-(291)] by

oxidn. with 20 pts. HNO_3 (D = 1.18) in s.t. at 220° for several hrs. (2) or with CrO_3/AcOH (2) see indic. refs.; from 1,3-dimethylbenzene-4,6-*bis*-(sulfonyl chloride) (1) with $SOCl_2$ in s.t. at 240° for 36 hrs. see (1).]

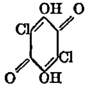
$Ag_2\bar{A}$, white ppt. (2), $Ba\bar{A}$, H_2O spar. sol. cold aq. but eas. sol. hot aq. (2).

Ⓓ **Dimethyl 4,6-dichloroisophthalate**: cryst. from dil. MeOH, m.p. 97–98° (1). [From $\bar{C}$ in MeOH on htg. (1).]

Ⓓ **4,6-Dichloroisophthaldianilide**: m.p. 205° (1). [From $\bar{C}$ on htg. with aniline (1).]

3:4965 (1) Pollak, Rudich, *Monatsh.* **43**, 221 (1922). (2) Claus, Burstert, *J. prakt. Chem.* (2) **41**, 558–560 (1890).

3:4970 2,5-DICHLORO-3,6-DIHYDROXY-BENZOQUINONE-1,4 $C_6H_2O_4Cl_2$ Beil. VIII - 379
(Chloranilic acid) $VIII_1$—



M.P. 283–284° s.t. (1)
282–284° s.t. (2)

Lustrous *red* lfts. with $2H_2O$ (3) (4) (lost at 100° or slowly on stdg. over conc. H_2SO_4 (3) (4)). — $\bar{C}$ on slow heating (even in s.t.) sublimes without melting; in s.t. inserted in bath or block preheated to about 278°, however, melts as stated above (1).

[For prepn. of $\bar{C}$ from chloranil (tetrachlorobenzoquinone-1,4) (3:4978) by actn. of dil. NaOH at 70–80° see (3) (2); for other methods see Beil. VIII-379.]

$\bar{C}$ is sol. in aq. yielding violet-red solns.; at 13.5 g. 100 pts. aq. dis. 0.19 pt., at 99° 1.4 pt. anhyd. $\bar{C}$ (3); addn. of HCl or H_2SO_4 ppts. $\bar{C}$ decolorizing soln. (5).

$\bar{C}$ behaves as strong dibasic ac. forming stable Na, K, Ba, Ag salts. — $Na_2\bar{A}.4H_2O$, dark red (7) triclinic (8) pr. sepg. on rapid cooling of warm soln. to 18° (6); loses $2H_2O$ over H_2SO_4 and becomes anhyd. at 110° (7). — $Na_2\bar{A}.3H_2O$, black cryst. sepg. from soln. above 35° (6). — $Na_2\bar{A}$; 100 pts. aq. at 21° dis. 1.06 g., at 99° 6.19 g. (3). — $Ag_2\bar{A}$, red ppt. spar. sol. aq. (8a).

$\bar{C}$ htd. in s.t. with conc. H_2SO_3 soln. for some hrs. (9) or treated with Sn + HCl (9) or Na/Hg (9) yields 3,6-dichloro-1,2,4,5-tetrahydroxybenzene (hydrochloranilic acid) [Beil. VI-1156], colorless cryst., no m.p. recorded but with AcCl in s.t. at 100° yielding tetra-acetyl deriv., colorless ndls. from alc. or by subl., m.p. 235° (9). [Use of insufficient SO_2 for reduction of $\bar{C}$ leads to pptn. of corresp. quinhydrone, fine black ndls. (9).] [For studies of oxidn.-reductn. potential of $\bar{C}$ see (2) (10) (11).]

$\bar{C}$ with alk. + I_2 — KI soln. yields (12) iodoform, m.p. 119°.

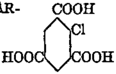
Ⓓ **2,5-Dichloro-3,6-dimethoxybenzoquinone-1,4** (dimethyl chloranilate) [Beil. VIII-380]: from $Ag_2\bar{A}$ + CH_3I (13) or from anhydrous $K_2\bar{A}$ + Me_2SO_4 (14); red pr. from C_6H_6 or $CHCl_3$, m.p. 141–142° (13) (14).

Ⓓ **2,5-Dichloro-3,6-diacetoxybenzoquinone-1,4** (chloranilic acid diacetate) [Beil. VIII-381]: from finely pdrd. $Ag_2\bar{A}$ + AcCl in dry ether (15); yel. ndls., m.p. 182.5° (15).

3:4970 (1) Michael, *Ber.* **28**, 1631 (1895) (2) Conant, Fieser, *J. Am. Chem. Soc.* **46**, 1866–1867 (1924). (3) Graebe, *Ann.* **263**, 24–27 (1891). (4) Jackson, MacLaurin, *Am. Chem. J.* **37**, 98–100 (1907). (5) Erdmann, *J. prakt. Chem.* (1) **22**, 285 (1841). (6) Valeur, *Ann. chim.* (7) **21**, 510–512 (1900). (7) Hesse, *Ann.* **114**, 304 (1860). (8) Pope, *J. Chem. Soc.* **61**, 583–584 (1892). (8a) Erdmann, *Ann.* **48**, 317 (1843). (9) Graebe, *Ann.* **146**, 32–36 (1868). (10) Conant, Lutz, *J. Am. Chem. Soc.* **46**, 1257 (1924).

(11) Schwarzenbach, Suter, *Helv. Chim. Acta* **24**, 626–628 (1941). (12) Jackson, Torrey, *Am. Chem J.* **20**, 429–430 (1898). (13) Kehrmann, *J. prakt. Chem.* (2) **40**, 370 (1888), **43**, 260 (1891). (14) Graebe, *Ann.* **340**, 248–249 (1905). (15) Nef, *Am. Chem. J.* **12**, 471–472 (1890); *J. prakt. Chem.* (2) **42**, 169–171 (1890).

3:4975 2-CHLOROBENZENETRICARBOXYLIC ACID-1,3,5 (Chlorotrimesic acid) $C_9H_5O_6Cl$ Beil. IX - 980 IX_1—



M.P. 285° (1) (anhydrous)
278° (2) (hydrate)

Ndls. or tbls. with 1 H_2O from aq. (2); very readily sol. cold aq. (1) (contrast (2)), extremely eas. sol. hot aq. (1) (2); eas. sol. alc, ether (2); insol. $CHCl_3$ (2). — Sublimes largely undecomposed (2).

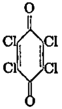
[For prepn. of $\bar{C}$ from chloromesitylene (3:8725) by oxidn. with aq. $KMnO_4$ either with or without $MgSO_4$ (63.5% yield) see (1); from 2-hydroxybenzenetricarboxylic acid-1,3,5 (hydroxytrimesic acid) [Beil. X-580] with PCl_5 (4 moles) followed by hydrolysis (with warm aq. or aq. alk.) of the intermediate *tris* acid chloride see (2).]

$Ba_3\bar{A}_2.7H_2O$ (from $\bar{C}$ + $BaCO_3$ (2)), fairly eas. sol cold aq. but spar. sol. in hot aq. (2).

[$\bar{C}$ on boilg. with aq alkali does *not* give chloride ion (2) but $\bar{C}$ with Zn + HCl (or H_2SO_4) or $\bar{C}$ in 10 pts. aq. with 10 pts. 4.5% Na/Hg yields trimesic acid (1:0559) (2)]

3:4975 (1) Davies, Wood, *J. Chem. Soc.* **1928**, 1126–1127. (2) Ost, *J. prakt. Chem* (2) **15**, 308–314 (1877).

3:4978 2,3,5,6-TETRACHLOROBENZOQUINONE-1,4 (Tetrachloro-*p*-benzoquinone; chloranil) $C_6O_2Cl_4$ Beil. VII - 636 VII_1-(347)



M.P. 292°	(1) (68)
291–292°	(2)
290° s.t.	(3) (4) (5)
290°	(6) (7)
289–290°	(37)
289°	(60)
288–290°	(8)
288°	(9)
285°	(10)
283–284°	(11) (12)

[*See also tetrachlorohydroquinone* (3:4941).]

Golden-yellow cryst. from AcOH, acetone, C_6H_6, toluene, or by sublimation. — For crystallographic data see (13) (14) (15).

$\bar{C}$ on careful htg. sublimes without melting (16); for purification of $\bar{C}$ by sublimation (4) under reduced press. (17) (18) see indic. refs.; for study of sublimation press. of $\bar{C}$ see (19).

$\bar{C}$ is insol. aq.; alm. insol. in cold alc.; sparingly sol. hot alc. but somewhat more readily in ether; $\bar{C}$ is sparingly sol. $CHCl_3$, CCl_4, CS_2; insol. lgr.

[For study of heat of formn. of $\bar{C}$ see (20); for studies of heat of combustion see (21) (22).]

[For studies of bactericidal properties of $\bar{C}$ (23) or toxicity of $\bar{C}$ (or its associated by-products or contaminants) (24) (25) (26) see indic. refs.]

$\bar{C}$ comprises the essential constituent (99% (27)) of the commercial fungicide "Spergon" [for studies on use of $\bar{C}$ as (seed) fungicide see (27) (28) (29) (30) (31) (32); for studies on toxicity of $\bar{C}$ in such use see (33)].

PREPARATION OF $\bar{C}$

$\bar{C}$ because of its great resistance to further oxidation is formed as the end product of the oxidation with *HCl + $KClO_3$* of a *very large number of aromatic organic compounds* [e.g., for a list of 16 such which do and 31 which do not give $\bar{C}$, see (34); for extension to 130 cases which do, see (35) cf. (36).]

$\bar{C}$ can also be prepared by a very large number of methods (see below): of these the best appear to be those from benzoquinone-1,4 (1:9025) using conc. HCl + 30% H_2O_2 at 60° (97% yield (37)) cf. (38), and from *p*-aminophenol by conversion with SO_2Cl_2 (10 moles) at 70° (6) or at 40–45° for 4 days (73% yield (1)) to *N,N*-dichloro-2,3,5,6-tetrachloro-4-aminophenol, m.p. 71.5° (6), and reaction of the latter with boilg. EtOH (1) (6) in pres. of an inert solvent (39) to give (80–85% overall yield from *p*-aminophenol (1)) of $\bar{C}$ of exceptional purity and free from 2,3,5-trichlorobenzoquinone-1,4 (3:4672).

From Various Phenols

From phenol. [For prepn. of $\bar{C}$ from phenol (1:1420) with conc. HNO_3 + fumg. HCl (i.e., with aqua regia) on htg. in open flask in direct sunlight (25% yield (17)) (40), or in fumg. HCl with Cl_2 followed by htg. with conc. HNO_3 at 100° for 20 hrs. (34% yield (17)) cf. (40), by electrolysis in HCl/AcOH (41), or by action of conc. HCl + $KClO_3$ (42) (43) (note, however, that this method gives (17) (44) (45) (46) (47) a product seriously contaminated with 2,3,5-trichlorobenzoquinone-1,4 (3:4672) q.v.) see indic. refs. — For prepn. of $\bar{C}$ from phenol-contg. industrial waste waters with Cl_2 in alk. soln. followed by oxidn. with HNO_3 see (48) (49) (50) (51) (52).]

From various halophenols. *From 2,4,6-trichlorophenol.* [For prepn. of $\bar{C}$ from 2,4,6-trichlorophenol (3:1673) with $ClSO_3H$ (53), with Cl_2 + fumg. H_2SO_4 followed by $ClSO_3H$ *(90% yield (54)), with aqua regia (17) (40), with HCl + $KClO_3$ (42) (55), with CrO_3/AcOH* (15), or with $K_2Cr_2O_7/H_2SO_4$ (15) see indic. refs. — Note also that many of the processes starting from phenol (above) doubtless pass through 2,4,6-trichlorophenol]

From pentachlorophenol. [For prepn. of $\bar{C}$ from pentachlorophenol (3:4850) with $ClSO_3H$ (53) (54), with cold fumg. HNO_3 (56) (57) (58), or with Cl_2 + conc. HCl at 100° (58) see indic. refs.]

From "hexachlorophenol." [For formn. of $\bar{C}$ from "hexachlorophenol" (hexachlorocyclohexadien-1,4-one-3) (3:3180) with conc. (68) or fumg. (69) HNO_3, with conc. H_2SO_4 at 100° (68) (69), with aq or HCl in s.t. at 160° (69), or with $AlCl_3$ (1/6 mole) in s.t at 160° (70) see indic. refs.]

From 2,4,6-triiodophenol. [For prepn. of $\bar{C}$ from 2,4,6-triiodophenol with Cl_2 in boilg. AcOH soln. (100% yield) see (10).]

From various nitroso- and nitro-phenols. [For prepn. of $\bar{C}$ from *p*-nitrosophenol in conc. HCl at 90° with Cl_2 see (59).]

[For formn. of $\bar{C}$ from *o*-nitrophenol (17) (40) (60), *p*-nitrophenol (17) (40) (60), 2,4,6-*trinitrophenol (picric acid) (17) (40) (61) with aqua regia, or from picric acid with Cl_2* (61) or Cl_2 + I_2 (62) in hot aq. soln., or from picric acid with HCl + $KClO_3$ (42) (47) see indic. refs.; for formn. of $\bar{C}$ from *p*-nitrophenol or 2,4-dinitrophenol with aq. NaOCl soln. see (63).]

From polyhydric phenols. *From resorcinol.* [For formn. of $\bar{C}$ from resorcinol (1:1530) with $ClSO_3H$ (40 wt. pts.) at 150–160° for 25 hrs. (note that much 2,3,5-trichlorobenzoquinone-1,4 (3:4672) is also formed) see (64) cf. (54).]

From hydroquinone. [For formn of $\bar{C}$ from hydroquinone (1:1590) with Cl_2 in AcOH (5), with Cl_2 + conc. HCl at 100° (65) (53), with aqua regia (4), with $ClSO_3H$ at 150–160° (8) see indic. refs.; for formn. of $\bar{C}$ from hydroquinone-pyridinium chloride with $SOCl_2$ (2) or from hydroquinone-2,6-*bis*-(sulfonyl chloride) with PCl_5 in s.t. at 140–150° for 6 hrs. (67) see indic refs.]

From pyrogallol. [For formn. of $\bar{C}$ from pyrogallol (1 1555) with $ClSO_3H$ at elevated temp. see (66)]

From various quinones. *From p-benzoquinone.* [For formn. of $\bar{C}$ from benzoquinone-1,4 (1.9025) with Cl_2 in conc. HCl (53) (65) with Cl_2 in AcOH (71) cf. (72), or with HCl + $KClO_3$ (42) see indic refs]

From the dichloro-p-benzoquinones. [For formn. of $\bar{C}$ from 2,3-dichlorobenzoquinone-1,4 (3:2855), from 2,5-dichlorobenzoquinone-1,4 (3:4470), or from 2,6-dichlorobenzoquinone-1,4 (3:3750) with Cl_2 in $CHCl_3$ see (73).]

From trichloro-p-benzoquinone. [For formn. of $\bar{C}$ from 2,3,5-trichlorobenzoquinone-1,4 (3:4672) with $Cl_2 + I_2$ + aq (47), or with Cl_2 + HCl (65), see indic. refs]

From various amines. [For formn. of $\bar{C}$ from aniline in 10% HCl by electrolytic oxidation (23% yield (9)) (74), with HCl + $KClO_3$ (75) (76), with $Na_2Cr_2O_7$ + HCl (89), or with aqua regia (60) see indic. refs. — For formn. of $\bar{C}$ from diphenylamine, 2,4-dichloroaniline, *m*-nitroaniline, aniline black, or phenylhydrazine with aqua regia see (60).]

[For formn. of $\bar{C}$ from *p*-phenylenediamine with aqua regia (60) (4), with $ClSO_3H$ (large excess) at 150–160° for 5 hrs. (77), with Cl_2 in AcOH (78), or with HCl + $KClO_3$ (3) see indic. refs.; from 2,6-dichloro-*p*-phenylenediamine with HCl + $KClO_3$ see (79).]

[For formn. of $\bar{C}$ from *o*-aminobenzoic acid (anthranilic acid) (42) (80), *m*-aminobenzoic acid (80), *p*-aminobenzoic acid (80), *l*-tyrosine (α-amino-β-(*p*-hydroxyphenyl)propionic acid) (81) with HCl + $KClO_3$ see indic. refs.; from sulfanilic acid (aniline-*p*-sulfonic acid) with aqua regia see (60).]

[For formn. of $\bar{C}$ from 2,3,5,6-tetrachloro-*p*-phenetidine by diazotization and boilg. see (82).]

From miscellaneous sources. [For formn. of $\bar{C}$ from 1,2,4,5-tetrachlorobenzene (3:4115) as by-product of nitration with fumg. HNO_3 see under (3:4115); from hexachlorobenzene (3:4939) on boilg. with mixt. of fumg. HNO_3 + conc. H_2SO_4 see (83); from *N*-nitro-2,4,6-trichloroaniline in dil alc. or AcOH soln. with HCl or H_2SO_4 see (84); from *N*-nitro-acet-2,3,5,6-tetrachloroanilide on boilg. in toluene or xylene see (85); from tetrachlorobenzoquinone-1,4-mono-(2,4,6-trichlorophenylimide) by H_2SO_4 hydrolysis see (86); from various azo dyes by oxidn. with NaOCl soln. at 0° see (87); from anisolesulfonic acid or phenetolesulfonic acid in aq. soln. with Cl_2 see (88); from nitrobenzene with $ClSO_3H$ (20 wt. parts) at 150° for 20 hrs. (95% yield) see (7)]

CHEMICAL BEHAVIOR OF $\bar{C}$

Reduction of $\bar{C}$

$\bar{C}$ upon reduction by a wide variety of reagents gives tetrachlorohydroquinone (3:4941) the text of which should be consulted for details.

Oxidation of $\bar{C}$

$\bar{C}$ is extremely stable to oxidizing agents in neutral or acid soln. and is unaffected by aqua regia or hot conc. HNO_3.

Behavior with Chlorine

[C̄ with MnO_2 + conc. HCl in s.t. at 180° for 10 hrs. adds 1 mole Cl_2 giving (45) hexachlorocyclohexen-2-dione-1,4 [Beil. VII-574], m.p. 89° (45).]

Behavior with Other Inorganic Reactants

In many of the reactions of C̄ with other reagents, 2 of the chlorine atoms are often replaced by other groups as exemplified below.

With aqueous alkali. C̄ with dil. aq. alk. at 70–80° readily replaces 2 chlorine atoms by hydroxyls giving (16) (3) (90) (91) (92) 2,5-dichloro-3,6-dihydroxybenzoquinone-1,4 (chloranilic acid) (3:4970), m.p. 282–284° s.t. (92).

With ammonia. [C̄ with alc. NH_3 on boilg. replaces 2 chlorine atoms by amino groups giving (75% yield (103)) (93) (94) 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloroanilamide) [Beil. XIV-144]. — Note, however, that C̄ with aqueous NH_4OH gives (16) 2,5-dichloro-3-amino-6-hydroxybenzoquinone-1,4 (chloranilamic acid) [Beil. XIV-250]]

With various salts. [C̄ with sodium azide as directed (95) (96) gives 2,5-dichloro-3,6-*bis*-azidobenzoquinone-1,4. — C̄ with $NaNO_2$ (2 moles) in conc. aq. soln. on warming gives (97) cf. (98) 2,5-dihydroxy-3,6-dinitrobenzoquinone-1,4 (nitranilic acid) [Beil. VIII-384, $VIII_1$-(683)]. — C̄ with KCN (2 moles) in 85% MeOH gives (99) 2,5-dihydroxy-3,6-dicyanobenzoquinone-1,4 (cyananilic acid) [Beil. X_1-(520)].]

[C̄ with warm dilute aq. acid $KHSO_3$ gives mainly (100) (101) the salt of 2,5-dichloro-3,6-disulfohydroquinone [Beil. XI-301], while with conc. solns. (100) or with neutral K_2SO_3 (101) (102) the main prod. is the salt of thiochronic acid [Beil. XI-302, XI_1-(80)], now (102) recognized as cyclohexadien-2,5-ol-4-one-1-pentasulfonic acid-2,3,4,5,6.]

With PCl_5. [C̄ with PCl_5 + PCl_3 in s.t. at 190–200° for 4 hrs. gives (95% yield (104)) cf. (43) hexachlorobenzene (3:4939); note also, however, that C̄ with PCl_5 + PCl_3 at 135–140° followed by treatment with aq. may also yield (45) (105) mono-(pentachlorophenyl)-phosphoric acid (monohydrate), m.p. 224° (105), and other products.]

Behavior of C̄ with Organic Reactants

With aromatic hydrocarbons. [C̄ with various aromatic hydrocarbons yields addition compounds: e.g., C̄ with 1,2,4,5-tetramethylbenzene (durene) (1:7195) in hot AcOH gives (106) (107) a red cpd. C̄.2 durene; C̄ with hexamethylbenzene (1:7265) gives from hot AcOH (108) violet-brown ndls. of a 1:1 cpd., m.p. 198–202° (108) (for further study of this prod see (109) (110)); C̄ with acenaphthene (1:7225) gives (111) (112) from AcOH (107) a violet 1:1 addn. cpd.]

With dienes and other unsaturates. C̄ with many dienes and other highly unsaturated compounds forms addn. products and/or gives color reactions.

[C̄ with cyclopentadiene (1:8030) in C_6H_6 in pres. of a little Me_3N gives (113) a 1:1 addn. cpd, yellowish ndls. from abs. alc., m.p. 146–146.5° (113) (corresp. dibromide with Br_2 in $CHCl_3$ in direct sunlight, lfts. from AcOEt, m.p. 269° (113)); note that in absence of Me_3N yield in 14 days is only 40%, in presence of Me_3N 100% (for study of cat. influence of Me_3N and of $CCl_3.COOH$ see (114)).]

[For study of color reactions of C̄ in $CHCl_3$ soln. with various trienes see (115) cf. (116) (117).]

[For studies of influence of C̄ on polymerization of styrene (1:7435) see (118) (119) (120); for study of effect of C̄ on polymerization or depolymerization of natural rubber see (121); for use of C̄ as vulcanization accelerator see (122).]

With *organic OH (or SH) reactants. With alcohols.* [C̄ in boilg. MeOH gradually treated with calcd. amt. 1% MeOH/KOH gives (123) (124) a mixt. of 2,5-dichloro-3,6-

dimethoxybenzoquinone-1,4 (chloranilic acid dimethyl ether) [Beil. VIII-380], dark red pr. from C_6H_6, m p. 141–142° (123), and 2,6-dichloro-3,5-dimethoxybenzoquinone-1,4 (isochloroanilic acid dimethyl ether) [Beil. VIII-387], dark red pr., m.p. 159° (125) (126), 157–158° (123), 155.5° (127). — Note, however, that C̄ with MeOH/NaOMe (5–6 moles) gives 2,5-dichloro-3,6-dimethoxybenzoquinone-1,4-*bis* (monomethyl acetal) [Beil. VIII-381] accompanied by tetrachlorohydroquinone (3:4941).]

With phenols. [C̄ (1 mole) with phenol (2 moles) in aq. KOH at 100° gives (128) 2,5-dichloro-3,6-diphenoxybenzoquinone-1,4 (chloranilic acid diphenyl ether) [Beil. VIII-380], dark red pr. from C_6H_6, m p. 243° (128). — C̄ (1 mole) with aq. K *p*-cresolate (2 moles) at 100° gives (129) 2,5-dichloro-3,6-di-(*p*-toloxy)benzoquinone-1,4 (chloranilic acid di-*p*-tolyl ether) [Beil. $VIII_1$-(681)], cryst. from toluene, m.p. 254–255° (129)]

With mercaptans. [C̄ (1 mole) with EtSH (4 moles) with EtOH/KOH (4 moles) as directed gives (95% yield (130)) 2,3,5,6-tetra-*kis*-(ethylthio)benzoquinone-1,4 [Beil. VIII-535], dark green ndls from alc., m.p. 90–91° (131).]

With thiophenols. [C̄ (1 mole) with C_6H_5SH in alk. soln. might be expected to yield 2,3,5,6-tetra-*kis*-(phenylmercapto)benzoquinone-1,4, but neither this reaction nor the expected product appears to have been reported. — However, various analogous cases are known: e.g., C̄ (1 mole) with *p*-thiocresol (4 moles) in AcOH at 100° for ½ hr. gives (132) 2,3,5,6-tetra-*kis*-(*p*-tolylthio)benzoquinone-1,4, cryst. from AcOH, m.p. 203° (132). — C̄ (1 mole) with *o*-nitrothiophenol in boilg. EtOH for 1 hr. gives (96) 2,3,5,6-tetra-(*o*)-nitrophenylmercapto)benzoquinone-1,4, no m.p. given.]

With organic amines. *General.* The behavior of C̄ with aliphatic amines appears to have been little studied from the structural viewpoint. [However, for studies on color reactions of C̄ with *prim.*, *sec.*, and *ter*-amines (or their salts) (133), for use of C̄ (in epichlorohydrin soln.) as a test for plasmochin (134) (135), or for use of C̄ in detection of $MeNH_2$, Me_2NH, or Me_3N and differentiation from NH_3 (136) (137), for use in spot test reactions of 38 different amines (147) see indic. refs.]

With primary aliphatic amines. [C̄ with $MeNH_2$ might be expected to give 2,5-dichloro-3,6-*bis*-(methylamino)benzoquinone-1,4 or even 2,3,5,6-tetra-*kis*-(methylamino)benzoquinone-1,4, but the reaction has not been reported and neither product is known.]

With primary aromatic amines. [C̄ with aniline in boilg. alc. refluxed 30 min gives (81% yield (138)) (100) (93) (139) 2,5-dichloro-3,6-dianilinobenzoquinone-1,4 [Beil. XIV-144, XIV_1-(421)], yel.-br. lfts. from C_6H_6 or nitrobenzene, m p. 292–293° (138), 290° (140), 288–290° (141); note that this product serves as bases for prepn. of many complex dyestuffs which cannot be discussed here. — C̄ with many other homologous and analogous primary aromatic amines behaves similarly.

[C̄ with phenylhydrazine in absol. alc. evolves N_2 and gives (10) a chlorine-contg prod., m.p. 229–230°, of undetermined structure.]

With various organometallic reactants. [C̄ (1 mole) in alc. with diethyl sodiomalonate (4 moles) in C_6H_6 gives (10% yield (142)) tetraethyl 2,5-dichloro-*p*-benzoquinone-3,6-dimalonate [Beil. X-940], yel. ndls. from alc., m.p. 132° (143).]

[For behavior of C̄ with ethyl sodio-acetoacetate see (144) (145), Beil. X-860, and Beil. X-935]

[For behavior of C̄ with excess C_6H_5MgBr see (146).]

Ⓟ Color tests for C̄. Of the large number of color tests shown by C̄ with various reactants, the following have been especially employed as preliminary tests for C̄ itself; note that for details, limitations, etc., the original references should be consulted.

With dimethylaniline. C̄ on warming with dimethylaniline gives intense violet color (Mulliken).

With ethyl cyanoacetate. C̄ with ethyl cyanoacetate (2–3 drops) + excess alc. NH_4OH (2–3 ml. of mixt. of 1 pt. abs. EtOH + 1 pt. conc. NH_4OH) gives intense bluish-violet coloration, changing to blue, green, and finally reddish brown (148). [Note that the reaction is also shown by certain other quinones, e.g., benzoquinone-1,4 (1:9025), *o*-toluquinone, thymoquinone, and naphthoquinone-1,4 (1:9040), but is *not* given by anthraquinone (1:9095), phenanthraquinone (1:9086), naphthoquinone-1,2 (1:9062), or 2,5-dichloro-3,6-diaminobenzoquinone-1,4 (chloranilamide) (148).]

With triphenylphosphine. C̄ with 20% soln. of $(C_6H_5)_3P$ in $CHCl_3$ gives (149) a wine-red color. [Note, however, that a similar behavior is also shown by 2,3,5-trichlorobenzoquinone-1,4 (3:4672) and certain other quinones (149).]

3:4978 (1) Eller, Lorenz, *Ber.* **58**, 494–497 (1925). (2) Koenigs, Greiner, *Ber.* **64**, 1047 (1931). (3) Graebe, *Ann.* **263**, 16–31 (1891). (4) Datta, *J. Am. Chem. Soc.* **36**, 1011–1013 (1914). (5) Datta, Bhoumik, *J. Am. Chem. Soc.* **43**, 313 (1921). (6) Eller, Klemm, *Ber.* **55**, 219, 223–224 (1922). (7) Pollak, Heimburg-Krauss, Katscher, Lustig, *Monatsh.* **55**, 373 (1930). (8) Pollak, Gebauer-Fülnegg, *Monatsh.* **47**, 115 (1926). (9) Erdélyi, *Ber.* **63**, 1200–1201 (1930). (10) King, McCombie, *J. Chem. Soc.* **103**, 225–226 (1913).

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905 (1927). (35) C

Feb. 4, 1913; *Cent.* **1913**, I 758; *C.A.* **7**, 2096–2097 (1913).

(41) Fichter, Glantzstein, *Ber.* **49**, 2473–2481 (1916). (42) Hofmann, *Ann.* **52**, 57–65 (1844). (43) Graebe, *Ann.* **146**, 8–18 (1868). (44) Bouveault, *Ann. chim.* (8) **13**, 142–144 (1908). (45) Zincke, Fuchs, *Ann.* **267**, 15–19, (1892). (46) Knapp, Schultz, *Ann.* **210**, 174–176 (1881). (47) Stenhouse

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Shvedova, Par

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38, 1817–1821 (1916).

(61) Stenhouse, *Ann.* **66**, 212 (1848). (62) Stenhouse, *Ann.* **145**, 362–364 (1868). (63)

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d. sci.
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–16 (1929), *Cent.* **1929,** II 2177; *C.A.* **23,**
1) **28,** 203 (1843). (76) Hofmann, *Ann.*
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(81) Städeler, *Ann.* **116,** 99–102 (1860). (82) Bures, Kovarovicova, *Časopis Českoslov. Lékárnictva* **10,** 197–202, 233–239 (1930); *Cent.* **1930,** II 2775; [*C.A.* **25,** 1816 (1931)] (83) Istrati, *Bull. soc. chim* (3) **3,** 184–186 (1890). (84) Orton, Pearson, *J. Chem. Soc.* **93,** 731 (1908). (85) Peters, Rowe, Stead, *J. Chem. Soc* **1943,** 372. (86) Bradfield, Cooper, Orton, *J. Chem. Soc.* **1927,** 2859. (87) Seyewetz, Chaix, *Bull. soc. chim.* (4) **41,** 333–335, 337 (1927). (88) Datta, Mitter, *J. Am. Chem Soc.* **41,** 2030–2032 (1919). (89) Elbs, Brunnschweiler, *J. prakt. Chem.* (2) **52,** 560 (1895). (90) Graebe, *Ann.* **146,** 30–32 (1868).

(91) Stenhouse, *Ann. Suppl.* **8,** 14–18 (1872). (92) Conant, Fieser, *J. Am. Chem. Soc.* **46,** 1866 (1924) (93) Knapp, Schultz, *Ann.* **210,** 183–189 (1881). (94) Laurent, *Ann.* **52,** 347–348 (1844). (95) Korczynski, *Bull soc. chim.* (4) **35,** 1189–1190 (1924). (96) Fries, Ochwat, *Ber.* **56,** 1302–1304 (1923). (97) Nef, *Ber.* **20,** 2028–2031 (1887). (98) Nef, *Am Chem. J.* **11,** 17–26 (1889). (99) Richter, *Ber.* **44,** 3472–3473 (1911); **45,** 1682 (1912) (100) Hesse, *Ann.* **114,** 306, 324, 327 (1860).

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(111) Haakh, *Ber.* **42,** oth, Bam-
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260–267 (1891). (125) Graet
Monatsh **49,** 186 (1928) (1
Jackson, Grindley, *Am. Chem*
Chem. Soc. **34,** 711 (1912). (1
(131) Grindley, Sammis, *A*
Monatsh. **58,** 133 (1931). (1
Sivadjian, *J. pharm. chim.* (8
(135) Schuleman, Schönhöfer,
Amoureux, *Bull. soc. chim. bio*
(137) Tsalpatani, *Bul Soc. S*
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2619; [*C.A.* **22,** 1585 (1928)].
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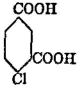
(141) Schütz, Buschmann, Wiss
38–42 (1891).
45, 65–66, 71–7
Ber. **64,** 1600–1
(148) Craven, *J. Chem. Soc.* **1940,**
1376–1377.

3:4980 4-CHLOROISOPHTHALIC ACID (4-Chlorobenzenedicarboxylic acid-1,3)



$C_8H_5O_4Cl$ Beil. IX - 837, IX$_1$-(372)

M.P.	295°	(1)
	294.5°	(2)
	293°	(3)
	290–292°	(4)
	280° u.c.	(5)

Colorless ndls. from hot aq. in which it is very spar. sol. requiring 130 pts. for soln. (4); eas. sol. alc., spar. sol. ether; insol. C_6H_6 or $CHCl_3$ (2).

[For prepn. of C̄ from 4-chloro-1,3-dimethylbenzene (3:8665) by oxidn. with aq. $KMnO_4$ (1) in pres. of $MgSO_4$ (2) see indic. refs.; from 2-chloro-5-methylphenyl methyl ketone (3), 2-chloro-5-methylbenzoic acid (6) (3:4615), or *α,β-bis*-(2-chloro-5-methylbenzoyl)ethylene (5) by oxidn. with $KMnO_4$ see indic. refs.; from sodium 1,3-dimethylbenzenesulfonate [Beil. XI-123, XI$_1$-(34)] with $SOCl_2$ in s.t. at 230°, followed by treatment with aq. alk., see (7); from 4-chloroisophthaldiamide (see below) by hydrolysis with boilg. aq. KOH see (4).]

—— Dimethyl 4-chloroisophthalate: unreported.

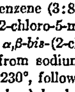
—— Diethyl 4-chloroisophthalate: unreported.

—— 4-Chloroisophthaldiamide: ndls., lfts., or pl. from 17 pts. boilg. aq., m.p. 232–233° (4). [From isophthalic acid-4-arsinic acid (1,3-dicarboxybenzenearsinic acid-4, 1,3$(HOOC)_2.C_6H_3.As(O)(OH)_2$, with PCl_5 at 110° for 3 hrs. followed by treatment in toluene soln. with NH_3 (4).]

3:4980 (1) Davies, Wood, *J. Chem. Soc.* **1928**, 1126. (2) Ullmann, Uzbachian, *Ber.* **36**, 1799 (1903). (3) Mayer, Freund, *Ber.* **55**, 2052 (1922). (4) Gough, King, *J. Chem. Soc.* **1930**, 690–691. (5) Conant, Lutz, *J. Am. Chem. Soc.* **47**, 891 (1925). (6) Scholl, Meyer, Keller, *Ann.* **513**, 298 (1934). (7) Farbwerke Meister Lucius & Brüning, Ger. 282,133, Feb. 15, 1915; *Cent.* **1915**, I 464.

3:4985 2,5-DICHLOROTEREPHTHALIC ACID (2,5-Dichlorobenzenedicarboxylic acid-1,4)

$C_8H_4O_4Cl_2$ Beil. IX -847, IX$_1$—



M.P.	306–306.5°	(1)
	305–306° cor.	(2)
	305°	(3)

Colorless ndls. from hot aq.; sublimes on cautious gradual htg.

[For prepn. of C̄ from 2,5-dichloro-1-methyl-4-isopropylbenzene (2,5-dichloro-*p*-cymene [Beil. V-423, V$_2$-(326)] by oxidn. with 20 pts. HNO_3 ($D = 1.15$) in s.t. at 180–200° for 10–12 hrs. (1) (3) see indic. refs.; from 2,5-dichlorocyclohexadiene-1,4-dicarboxylic acid-1,4 (2,5-dichloro-3,6-dihydroterephthalic acid) [Beil. IX-785] in 12% yield by short boilg. with 20% HNO_3 (some 2,5-dichloro-3-nitroterephthalic acid is also formed) see (4) (2); from 2,5-dichloro-1,4-*bis*-(trichloromethyl)benzene (5) by hydrolysis with H_2SO_4 (66° Bé) at 70–80° see (5).]

II

BOILING POINTS

RY PRESSURE

r than 1.1500

.400,

COCl$_2$ Fe2. III - 13

III$_2$-(7)

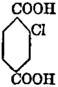
III$_2$-(12)

D_4^{11} – 1.392 (1)

See Note 2.

3:4990 (1) Klingste
Cent. **1928**, I 504;
2104 (1931). (3)
Sci. Kyoto Imp. Un
Nörr, *Ber.* **33**, 726
Hendrick, Bilicke,
Linden, *Ber.* **45**, 2
Matthews, *J. Chem. Soc.* **59**, 165–172 (1891).

3:4995 CHLOROTEREPHTHALIC ACID (2-Chlorobenzenedicarboxylic acid-1,4)



$C_8H_5O_4Cl$ Beil. IX-847, IX_1—

M.P. 320° (1) (2)
Above 300° (3)
300° (4)

Cryst. from hot aq. (3), very dil. alc., (3) or 50% alc. (7); sol. in much hot aq., eas. sol. alc. or ether.

[For prepn. of $\bar{C}$ from 2-aminobenzenedicarboxylic acid-1,4 [Beil. XIV-558, XIV_1-(637)] via diazotization and use of Cu_2Cl_2 reactn. see (3); from 3-chloro-1-methyl-4-isopropylbenzene (3-chloro-*p*-cymene) (3:8770) by oxidn. with 15 pts. boilg. HNO_3 ($D = 1.39$) for 1 day (other prods. are also formed) see (4); from 3-chloro-4-acetylbenzoic acid (1), from 2-chloro-4-acetylbenzoic acid (2), or from 3-chloro-4-methylphenyl methyl ketone (8) by oxidn. with alk. $KMnO_4$ see indic. refs.; from 2-chloro-4-carbamidobenzoic acid (5) by hydrolysis with boilg. 25% NaOH see (5); from 2-chloro-4-methylbenzotrichloride (6) by hydrolysis with H_2SO_4 (66° Bé) at 70–80° see (6).]

$Ag_2\bar{A}$; pptd. from soln. of $(NH_4)_2\bar{A}$ by addn. of $AgNO_3$ (3).

[$\bar{C}$ with PCl_5 (3) or with $SOCl_2$ in pres. of $SbCl_5$, $AlCl_3$, or $SnCl_4$ (7) yields chloroterephthaloyl (di)chloride, b.p. 154–155° at 19 mm. (7).]

[$\bar{C}$ on nitration with HNO_3/H_2SO_4 at 65° yields (7) 2-chloro-5-nitrobenzenedicarboxylic acid-1,4, cryst. from 50% alc., m.p. 265° (7), 263–264° (8) (this prod. is also obtd. from 2-chloro-4-methyl-5-nitrophenyl methyl ketone (8) by oxidn.).]

Ⓓ **Dimethyl chloroterephthalate:** lfts. from MeOH, m.p. 60° (6) (3), 59–60° (4). [From $\bar{C}$ in MeOH with HCl gas or from $Ag_2\bar{A}$ with MeI (3).]

—— **Diethyl chloroterephthalate:** oil (3).

—— **Chloroterephthaldiamide:** cryst. from dil. alc., m.p. above 300° (3). [From chloroterephthaloyl (di)chloride (above) with $(NH_4)_2CO_3$ (3).]

3:4995 (1) Ganguly, LeFevre, *J. Chem. Soc.* **1934**, 851. (2) Ganguly, LeFevre, *J. Chem. Soc.* **1934**, 854. (3) Ahrens, *Ber.* **19**, 1637–1639 (1886). (4) Fileti, Crosa, *Gazz. chim. ital.* **18**, II 311, 313 (1888). (5) Magidson, Trawin, *Ber.* **69**, 540 (1936). (6) I.G., French 663,791, Aug. 26, 1929; *Cent.* **1929**, II 2731–2732. (7) I.G., French 810,595, March 24, 1937; *Cent.* **1937**, I 5048; *C.A.* **32**, 592 (1938). (8) Mayer, Albert, Schön, *Ber.* **65**, 1296, 1298–1299 (1932).

CHAPTER XII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(1.5000–1.5499)

1.5000 PHOSGENE (Carbonyl chloride) $COCl_2$ B-2, III – 13; III_1–(7); III_2–(12)

B.P.			F.P.		
[illegible]	at [illegible] mm. (1)		[illegible]	(2)	$D_4^{[illegible]}$ = 1.392 (1)
[illegible]	at [illegible] mm. (2)		–126°	(?)	
[illegible]	at [illegible] mm. (3)		–127.5° (?)		See Note 2
[illegible]	at 760 mm. (4)		–128°	(?)	
[illegible]	at 760 mm. (?)				
[illegible]	at [illegible] mm. (6)				
[illegible]	at 760 mm. (?)				

See Note 1

Note 1. [illegible]

Note 2. [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

solvents at pressures below 1 atm. see (32) cf. (33); for patent on removal of C̄ from contaminated drinking water by extraction with org. solvents see (34)].

[For technical papers (36) (37) (38) (39) (40) (41) (42) (43) (44) (45) and patents (46) on adsorption of C̄ by various forms of carbon see indic. refs.]

[For influence of C̄ in extinction of H/O flames see (47).]

PHYSIOLOGICAL ASPECTS OF C̄

C̄ is more than ten times as toxic as Cl_2. An atmosphere contg. 1 part by vol. of C̄ in 6000 may cause lung injuries in 2 min., 1 part in 30,000 is very dangerous, and 1 part in 200,000 is probably fatal for exposures of 30 min. The maximum permissible concn. for prolonged exposure is about 1 p.p.m., i.e., 0.004 mg./l. (48).

The least detectable odor of C̄ is 5.6 p.p.m., the least concn. that affects the throat is 3.1 p.p.m., the least concn. that causes irritation of the eyes is 4.0 p.p.m., the least concn. that causes coughing is 4.8 p.p.m. (48) (49). A concn. of 0.02–0.05% is lethal to most animals in a short time, a concn. of 0.0025% is dangerous for exposures of 30–60 min., and the maximum concn. to which animals can be exposed for several hours without serious effects is 0.0001% or 1 p.p.m. (48) (50).

[For report of industrial accidents from C̄ (51), for legal (British) aspects of industrial poisoning by C̄ (52), for toxicology and treatment of poisoning by C̄ (53), for immunization against C̄ (54), for variations in toxicity of C̄ for small animals with duration of exposure (55) see indic. refs.]

[For studies relating to chemical warfare aspects of C̄ with respect to foodstuffs see (56) (57).]

USES OF C̄

Apart from the uses of C̄ as a chemical warfare agent (above), many chemical utilizations are indicated below under its chemical behavior. [In addition will be mentioned here a few further examples as follows: for use of mixt. of C̄ + HF for cracking of hydrocarbon oils see (58); for use as dehydrating agent in conversion of amides to corresp. nitriles see (59); for use in sepn. of Pt metals see (60).]

DETECTION OF C̄

C̄ may be detected by its characteristic odor (see above) and by various color reactions of which the following represent the more important types.

For detection of C̄ by the yellow or orange color produced by reaction with Harrison's reagent (a soln. in EtOH (100 ml.) of *p*-dimethylaminobenzaldehyde [Beil. XIV-31, XIV_1-(360)] (5 g.) (for prepn. see (61)) and of diphenylamine [Beil. XII-174, XII_1-(163)] (5 g.)) see (62) (63) (64) (65) (66) (67) (68) (69) (70) (71) (83); note that this test suffers interference from HCl, Cl_2, $ClSO_3H$, $TiCl_4$, chloromethyl chloroformate (3:5275), diphosgene (3:5515), and triphosgene (3:1915); for application of this reagent in an absorptive tube see (72) cf. (73).

For detection of C̄ by green color imparted to a test paper impregnated with a xylene soln. of 0.5% 6-nitroso-3-dimethylaminophenol (4-dimethylamino-*o*-benzoquinoneoxime-1) [Beil. XIV-131] and a xylene soln. of 0.5% *m*-diethylaminophenol [Beil. XIII-408, $XIII_1$-(130)] see (74) (75) (76).

For spot test detection of C̄ by use of phenylhydrazine cinnamate (for prepn. see (77)) in $CHCl_3$ or CCl_4 followed by treatment with 1% $CuSO_4$ soln. to give a red-violet color from the 1,5-diphenylcarbohydrazide [Beil. XV-292, XV_1-(72)] produced see (78).

For study of detection of C̄ with resorcinol (1:1530) or vanillin (1:0050) see (79); by

indirect use of the Gilman color test for RMgX compounds see (80) cf. (81); for study of utility of various dyestuffs in detection of $\bar{C}$ see (82).

DETERMINATION OF $\bar{C}$

Methods for the quant. detn. of $\bar{C}$ may be classified under three main types according to whether they are based upon hydrolysis, reaction with alkali iodides, or reaction with aniline.

Detn. by methods based on hydrolysis. [For studies of methods based upon alkaline hydrolysis of $\bar{C}$ and subsequent detn. of resultant chloride ion see (83) (84) (85) (86) (87) (88) (89) (90); for especial criticism of this method see (91).]

Detn. by reaction with alkali iodide. [For studies of methods based upon reaction of $\bar{C}$ with NaI (92) (91) or KI (93) in acetone followed by thiosulfate titration of the liberated I_2 see indic. refs.]

Detn. by reaction with aniline. [For study of methods based upon reaction of $\bar{C}$ with aniline and gravimetric estn. of the resultant N,N'-diphenylurea (carbanilide) (94) (95) cf. (91) or titration of the residual aniline HCl in the filtrate (96) see indic. refs.]

Related topics. [For detn. of small amts. Cl_2 in pres. of $\bar{C}$ (97), of HCl in $\bar{C}$ (98) (85), for analysis of mixts. of $\bar{C} + Cl_2 + NOCl$ (99), for anal. of mixts. of $\bar{C}$ with CO, CO_2, Cl_2, CCl_4, C_2Cl_6 (88) (86), for anal. of industrial $\bar{C}$ (89), or for detn. of $\bar{C}$ in air by means of an ultraviolet photometer (R. + H. Tri-Per Analyzer) (100) see indic. refs.]

PREPARATION OR FORMATION OF $\bar{C}$

From CO + Cl_2. The photochemical reaction of CO with Cl_2 to yield $\bar{C}$ was the method by which it was first prepared in 1812 (9) (for extensive history see (10)). Over the years the reaction has been very extensively studied. The more important earlier reports include those of Wilm and Wischin (101), Wildermann (102), Dyson and Hardin (103), Weigert (104), Coehn and Becker (105), Chapman and Gee (106), etc. Since 1920 the number of studies of this reaction has so greatly increased as to preclude in this text any detailed analysis; however, the following references ((107)–(134), incl.) arranged in receding chronology will be found fruitful from one viewpoint or another.

[For studies on formn. of $\bar{C}$ from CO + Cl_2 in dark at 349–452° (135) in liq. medium (145), or over cat. such as Pt at 300–400° (136), activated carbon (6) (137), or $AlCl_3$ at 30–35°, or in $CHCl_3$ soln. (138) see indic. refs. — For formn. of $\bar{C}$ from CO + NOCl over activated carbon at 100–250° see (139) cf. (137).]

[For formn. of $\bar{C}$ from CO passed over heated AgCl (140) (141), over $CuCl_2$, $PbCl_2$, or $NiCl_2$ at 450–750° (141), over heated $AuCl_3$ (142), or through boilg. $SbCl_5$ (143), or over chlorides of Pt metals (144) see indic. refs.]

From various chlorinated hydrocarbons. *From CCl_4.* [For studies on formn. of $\bar{C}$ from CCl_4 (3:5100) during use of latter as fire extinguisher see (146) (84) cf. (147) (368); for patents on repression of formn. of $\bar{C}$ in such use see (148) (149) (150) cf. (368); for formn. of $\bar{C}$ from CCl_4 fire extinguishers on Mg see (151); for phosgene content of smoke from Berger mixt. (Zn + chlorohydrocarbons) see (152).]

[For formn. of $\bar{C}$ from CCl_4 with O_2 in light of 2537 Å (153) or with atomic oxygen (154) see indic. refs.]

[For formn. of $\bar{C}$ from CCl_4 by chemical oxidizing agents such as O_2 over white-hot Pt (155), air over $CuCl_2$ or $FeCl_3$ at elev. temp. (156), GeO_2 (157), chromic acid (1) (158), pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (158) (159) (160) (161) (162) (163) see indic. refs.]

[For formn. of $\bar{C}$ from CCl_4 by passing with CO_2 over pumice at 350° (164), by htg. with

ZnO at 200° (164), with P_2O_5 at 200–220° for 2 days (165), or over gypsum at 900° (166), or even by htg. with a little aq. in s.t. at 250° (220) see indic. refs.]

From $CHCl_3$. [For an extensive account of formn. of $\bar{C}$ from $CHCl_3$ (3:5050) by oxidn. in air and light see (167). Note that such oxidn. is not effected by air in absence of light, nor by light in absence of air (168). With limited air in sunlight $CHCl_3$ reacts according to equation $CHCl_3 + O \rightarrow COCl_2 + HCl$, but with excess air in sunlight in sense $2CHCl_3 + 5O \rightarrow 2CO_2 + 3Cl_2 + H_2O$ (169). Note that $CHCl_3$ + air over dry KOH gives some $\bar{C}$ (170). For studies on photochem. oxidn. of $CHCl_3$ (171) in tropical sunlight (172) including search for possible intermediate peroxides (173) (174) see indic. refs. For studies of Cl_2-sensitized photochem. oxidn. of $CHCl_3$ see (175) (176) (177). For oxidn. of $CHCl_3$ by atomic oxygen see (154).]

[For formn. of $\bar{C}$ from $CHCl_3$ (3:5050) by shaking with siloxen + excess O_2 (178), by action of O_3 (179) (180), by passing over CuO at 350–550° (181) or gypsum at 900° (166), with $K_2Cr_2O_7 + H_2SO_4$ (1) (158), with $ClSO_3H$ at 120° (187), or during explosion of $CHCl_3$ with alkali metals (182) see indic. refs.]

From $Cl_2C{=}CCl_2$. [For formn. of $\bar{C}$ from tetrachloroethylene (3:5460) during Cl_2-sensitized photochem. oxidn. see (183) (184) (185).]

From $Cl_2C{=}CHCl$. [For formn. of $\bar{C}$ from trichloroethylene (3:5170) with air or O_3 see (186).]

From various compounds containing the trichloromethyl group. [For formn. of $\bar{C}$ from trichloroacetaldehyde (chloral) (3:5210) by Cl_2-sensitized (188) or Br_2-sensitized (189) photochem. oxidn. with O_2 at 70–90°, with Cl_2 in sunlight (190), or with $AlCl_3$ on warming (191) see indic. refs.]

[For formn. of $\bar{C}$ from trichloroacetic acid (3:1150) on htg. with $ZnCl_2$ (192), on illuminating dry acid in pres. of air (193), or on electrolysis of aq. soln. (194) see indic. refs.; from trichloroacetyl chloride (3:5420) at 600° (195); from trichloroacetonitrile in air (196); from trichloroacetyl hydrogen peroxide on warming (200); from trichlorobromomethane + Br_2 + O_2 in light (197) see indic. refs.]

[For formn. of $\bar{C}$ from di-(trichloromethyl) carbonate (triphosgene) (3:1915) on distn. (198), htg. at 200° in s.t. (199), or on mixing with charcoal and htg. just above m.p. (78°) (198) see indic. refs.; from trichloromethyl chloroformate (diphosgene) (3:5515) on htg. above 300° (200) (209) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (198); from methyl trichloromethyl carbonate [Beil. III-17, III_1-(8), III_2-(15)], b.p. 57–58° at 17 mm. (204), D_4^{17} = 1.5228 (204), n_D^{17} = 1.4487 (204), on boilg. at ord. press. (202) or on warming with $AlCl_3$ (203) (204); from ethyl trichloromethyl carbonate, b.p. 78° at 19 mm. (204), D_4^{20} = 1.4205 (204), n_D^{20} = 1.4450 (204), or from *n*-propyl trichloromethyl carbonate, b.p. 93° at 12 mm. (204), D_4^{20} = 1.359 (205), n_D^{20} = 1.4451 (205), on warming with $AlCl_3$ (203); from isoamyl trichloromethyl carbonate, b.p. 120° at 23 mm. (204), D_4^{20} = 1.2644 (204), n_D^{20} = 1.4466 (204), phenyl trichloromethyl carbonate [Beil. VI_1-(88)], m.p. 70.5° (204), or *p*-tolyl trichloromethyl carbonate (206) on warming with aq. (but not with aq. NaOH) (206); from *bis*-(trichloromethyl) oxalate [Beil. III-17] at 350–400° (207); or from trichloromethyl perchlorate (208) see indic. refs.]

[For formn. of $\bar{C}$ from trichloronitromethane (chloropicrin) [Beil. I-76, I_1-(20), I_2-(41)] in u.v. light (210), on boilg. (at 112°) under ord. press. (211), on passing with HCl over pumice at 400° (212), or on treatment with fuming H_2SO_4 (20% SO_3) at 100° (213) see indic. refs.]

From miscellaneous sources. [For formn. of $\bar{C}$ from CO_2 + CCl_4 (3:5100) + cat. at elevated temp. (225), from CS_2 with aqua regia (214) or Cl_2O (215); from COS with Cl_2 at red heat (1); from COS over fused $CuCl_2$ (1) or through boiling $SbCl_5$ (1); from thiophosgene with air or O_2 under various conditions (216); from anhydrous Na_2CO_3 with

PCl_5 (217); from pentachloropropionyl chloride (3:0470) with $AlCl_3$ at 60° (218); from oxalyl (di)chloride (3:5060) at 600° or with $AlCl_3$ in CS_2 on warming (219) see indic. refs.]

CHEMICAL BEHAVIOR OF Ĉ

Pyrolysis of Ĉ. Ĉ on heating above 300° decomposes in two ways: (1) into $CO + Cl_2$ (CO equilibrium) and (2) into $CO_2 + CCl_4$ (CO_2 equilibrium). The extent of these reactions together with the influence of various factors has been extensively studied. [For a concise summary of earlier work see the review of Dyson (11); for many important details see the original references represented by (225) (221) (222) (5) (135) (6) (223) (224).]

Photochemical decompn. of Ĉ. [Ĉ on exposure to short-wave u.v. light decomposes yielding (105) (226) $CO + Cl_2$; for more recent studies of this photochem. decompn. see (227) (228) (229) (230) (231); for application to problem of separation of isotopes of Cl_2 see (232).]

Electrolysis of Ĉ. [Ĉ or a soln. of $AlCl_3$ in Ĉ upon electrolysis gives (233) $CO + Cl_2$.]

Behavior of Ĉ with Inorganic Reactants

Reduction of Ĉ. [Ĉ + H_2 in u.v. light at 10° gives CO + HCl + traces of formaldehyde (1:0145) but at 80° gives $CO + CO_2 + CH_4$ + HCl (234). — Ĉ + H_2 over Pd or Ni on pumice, or over vanadium carbide, at 300–450° gives (235) cf. (236) CO + HCl + small amts. formaldehyde (1:0145) cf. (229).]

Oxidation of Ĉ. [For study of photochem. oxidn. of Ĉ see (230).]

Hydrolysis of Ĉ. Contrary to earlier reports Ĉ with aq. is almost instantly hydrolyzed but the rate is influenced by the manner in which contact is effected and whether the aq. is in vapor or liquid state. [For studies on the hydrol. of Ĉ see (237) (4) (96) (238); for study of rate of hydrolysis in dioxane at 25° (239) or in toluene at 25° and at 45° (240) see indic. refs.]

Behavior of Ĉ with metal oxides, sulfides, or phosphates. [Ĉ with metallic oxides on htg. at 250–600° (depending upon the metal) gives the corresp. metal chloride which in some cases, e.g., $FeCl_3$, $ThCl_4$, readily sublimes in pure form; for examples of this reaction see (211) (212) (213); for use in prepn. of $AlCl_3$ see (219).]

[Ĉ on htg. with metal sulfides gives (216) COS [Beil. III-131, III_1-(61), III_2-(101)], b.p. −50.2° (211), f.p. −138.2° (214) (use with CdS in prepn. (215)), and the metal chloride cf. (211).]

[Ĉ on htg. with certain phosphates (217) gives $CO_2 + POCl_3$ + metal chloride (use in prepn. of $POCl_3$ (218)).]

Analogs of Ĉ. *Carbonyl fluoride.* [This compound, b.p. −83.1° (250), m.p. −114.0° (250), has been prepd. from AgF_2 + CO (250), F_2 + CO (251) cf. (250), or from acetone with F_2 (252), but has not been reported from Ĉ. Note that Ĉ with HF at 80° and 280 lb./sq. in. in Cu bomb gives (25–50% yield (253)) carbonyl chlorofluoride, COClF, b.p. −42°, m.p. 138° (253).]

Carbonyl bromide. [Ĉ with BBr_3 at 150° (254) or with $AlBr_3$ (255) gives carbonyl bromide [Beil. III-29, III_1-(9), III_2-(7)], but this prod. is better prepd. from CBr_4 by oxidn. with conc. H_2SO_4 (256) (257) (258) (for study of photochemical oxidn. see (259)); for studies of structure (26) and pyrolysis (260) (261) (262) see indic. refs.]

Carbonyl cyanide. [This compound, b.p. 65.0–65.5° (263), D_4^{20} = 1.124 (263), n_D^{20} = 1.3919 (263), has been prepd. from acetonedicarboxylic acid (1:0485) by conversion (264) to diisonitrosoacetone [Beil. I-806, I_1-(413)], thence to diacetyl-di-isonitrosoacetone (265), then acetoxime acetyl cyanide (263) which was then pyrolyzed at 160–180° and

210–220 mm. (263) cf. (265). For formn. using propionyl (instead of acetyl) derivatives see (266).]

Behavior of $\bar{C}$ with inorganic acids. [$\bar{C}$ with HF as directed (250) (see analogs of $\bar{C}$ above) gives carbonyl chlorofluoride. — $\bar{C}$ with HBr does not react even at 200° (267). — $\bar{C}$ as liq. does not react with HI, but $\bar{C}$ as gas reacts with HI gas even at room temp. with sepn. of I_2 (267).]

Behavior of $\bar{C}$ with inorganic salts. [$\bar{C}$ with KI or NaI in acetone solns. gives $CO + I_2$ (use in detn. of $\bar{C}$ (91) (92) (93)).]

[The behavior of $AlCl_3$ with $\bar{C}$ has been extensively studied; for studies of solns. of $AlCl_3$ in liq. $\bar{C}$ from viewpoint of vapor pressure (268), density (269), and conductance (270) see indic. refs. — For general studies of liq. $\bar{C}$ as solvent (271) (272) including studies on system $\bar{C} + Cl_2$ (273) and on phosgeno salts such as calcium phosgeno-aluminate (274) (275) and others (276) see indic. refs.]

Behavior with various inorganic nitrogen compounds. *With NH_3.* [$\bar{C}$ in lgr. (277) or C_6H_6 (278) gives urea, biuret, cyanuric acid, cyamelide, ammelide, etc.; $\bar{C}$ as gas with NH_3 as gas gives urea (279) cf. (280) (143), guanidine, cyanuric acid (281), and cyamelide (282). — For reaction of $\bar{C}$ in toluene soln. with aq. NH_4OH as a source of isocyanic acid see (283). — Note also that $\bar{C}$ with sodamide reacts in cold in sense $COCl_2 + 3NaNH_2 \rightarrow NaNCO + 2NaCl + 2NH_3$, but at about 250° in sense $COCl_2 + 5NaNH_2 \rightarrow Na_2N{-}C{\equiv}N + 2NaCl + NaOH + 3NH_3$ (284).]

[$\bar{C}$ with NH_4Cl at elevated temps., e.g., 200–400°, gives (285) (286) carbamyl chloride, $NH_2.CO.Cl$ [Beil. III-31, III_1-(15)], b.p. 61–62° dec. (285). — For study of analogous carbamyl fluoride and carbamyl bromide (previously unknown) see (287).]

With hydroxylamine. [For studies on behavior of $\bar{C}$ with NH_2OH see (288) (289)]

With hydrazine: [$\bar{C}$ with 1 mole hydrazine would be expected to give *N*-aminocarbamyl chloride, $NH_2.NH.CO\,Cl$, but this compound appears to be unknown; $\bar{C}$ with 2 moles hydrazine should yield *N,N'*-diaminourea (carbohydrazide) [Beil. III-121, III_1-(57), III_2-(96)], but this compound has not been reported as prepd. by this method.]

Behavior of $\bar{C}$ with Organic Reactants

With hydrocarbons. [For studies on photochem. reaction of $\bar{C}$ with alkanes (290) or with cycloalkanes (291) or with aliphatic or alicyclic acid chlorides (292) as a means of replacement of hydrocarbon H atoms by the CO.Cl group see indic. refs. — For reaction of $\bar{C}$ with satd. nonaromatic hydrocarbons in pres. of cat. yielding ketones see (293). — Note also that $\bar{C}$ with $CH_4 + H_2$ + cat. is claimed (236) to give acetaldehyde (1:0100).]

$\bar{C}$ with aromatic hydrocarbons in pres. of a Friedel-Crafts' type cat. condenses according to conditions with either one or two moles of hydrocarbon yielding, respectively, the corresp. acid chloride or ketone. No attempt can be made here to collect the reported cases of these types since the many acid chlorides contained in this book afford numerous examples.

[$\bar{C}$ with ethylene + $AlCl_3$ in CS_2 adds to the unsatd. linkage giving (295) (296) (297) (298) β-chloropropionyl chloride (3:5690) although the method has been questioned (299) (300). — $\bar{C}$ with propylene + $AlCl_3$ as directed (301) gives β-chloroisobutyryl chloride (3:9101).]

[$\bar{C}$ with acetylene (302) or acetylene homologs (303) gives complex condensation products suitable for molding.]

With alcohols. $\bar{C}$ with alcohols reacts according to circumstances with either 1 mole alcohol giving the corresponding chloroformate (chlorocarbonate) esters, or with 2 moles alcohol giving the corresponding carbonate ester. The countless known cases cannot here be cited in detail but the following examples are given; see also the summary of Dyson (308).

$\bar{C}$ with MeOH (1:6120) gives (304) methyl chloroformate (3:5075) q.v. and/or dimethyl carbonate (1:3046); $\bar{C}$ with EtOH (1:6130) gives ethyl chloroformate (3:7295) q.v and/or diethyl carbonate (1:3150); $\bar{C}$ with *n*-PrOH (1:6150) gives *n*-propyl chloroformate (3:7540) q.v. and/or di-*n*-propyl carbonate (1:3373); $\bar{C}$ with isopropyl alcohol (1:6135) gives isopropyl chloroformate (3:7405) q.v. and/or di-isopropyl carbonate (1:3261); $\bar{C}$ with *n*-butyl alcohol (1:6180) gives *n*-butyl chloroformate (3:7980) q.v. and/or di-*n*-butyl carbonate (1:3626), $\bar{C}$ with isobutyl alcohol (1:6165) gives isobutyl chloroformate (3:7760) q.v. and/or di-isobutyl carbonate (1:3501), $\bar{C}$ with *n*-AmOH (1:6205) presumably gives *n*-amyl chloroformate (3:9380) q.v., but di-*n*-amyl carbonate appears to be unreported; $\bar{C}$ with isoamyl alcohol (1:6200) gives isoamyl chloroformate (3:8215) q.v. and/or di-isoamyl carbonate (1:3937).

$\bar{C}$ with allyl alcohol (1:6145) gives allyl chloroformate (3:7487) q.v. and/or diallyl carbonate; $\bar{C}$ with cyclohexanol (1:6415) gives cyclohexyl chloroformate (3:5770) q.v.; $\bar{C}$ with benzyl alcohol (1:6480) gives benzyl chloroformate (3:9565) q.v. — [For analogous reaction of $\bar{C}$ with unsatd. monohydric alcohols such as methallyl alcohol, crotyl alcohol, etc., see (305).]

$\bar{C}$ with *monohydroxyethers* gives analogous products: e.g., $\bar{C}$ with β-methoxyethanol (1:6405) gives β-methoxyethyl chloroformate (3:9140) q.v.; $\bar{C}$ with β-ethoxyethanol (1:6410) gives β-*ethoxyethyl chloroformate* (3:9280) *q.v.* — [*For reaction of* $\bar{C}$ *with* polyhydroxyethers such as diethylene glycol (1:6525), triethylene glycol (1:6538), tetraethylene glycol, *etc., giving corresp. bis-(chloroformates), see* (306).]

[For study of behavior of $\bar{C}$ toward various alkali alkoxides see (307).]

[*Note that* $\bar{C}$ *as liq. reacts with enol form of acetone (1:5900) in* ½ hr. at room temp. giving (330) isopropenyl chloroformate (3:7358).]

With phenols. The reaction of $\bar{C}$ with phenols is more sluggish than with alcohols, and the corresp. diaryl carbonates are usually obtained from $\bar{C}$ with 2 moles of the corresponding sodium phenolate cf. (308).

[$\bar{C}$ (as liquid) with phenol (1:1420) in s.t. at 140–150° (309), or $\bar{C}$ in toluene (310) or trichloroethylene (3:5170) (311) with aq. phenol (311) or aq. Na phenolate (310), or $\bar{C}$ with Na phenolate in toluene (312), or $\bar{C}$ with 10% aq. Na phenolate at 30° (313) gives (yields: 45% (312), 44% (313)) phenyl chloroformate [Beil. VI-159, VI_1-(88), VI_2-(157)], b.p. 97–98° at 25 mm. (310), 83–84° at 12 mm. (313), $n_D^{11} = 1.5180$ (313); for use as acylating agent see (314).]

[$\bar{C}$ in toluene shaken with a soln. of *o*-cresol (1:1400) in aq. NaOH (310) (315) gives *o*-tolyl chloroformate [Beil. VI-356], b.p. 119° at 35 mm. (310), 114° at 25 mm. (310). — $\bar{C}$ in toluene shaken with a soln. of *m*-cresol (1:1730) in aq. NaOH (315) gives *m*-tolyl chloroformate [Beil. VI-379], b.p. 103° at 22 mm. (315). — $\bar{C}$ in toluene shaken with a soln. of *p*-cresol (1:1410) in aq. NaOH (315), or $\bar{C}$ passed as gas into aq. Na *p*-cresolate below 10° (316), gives (78–80% yield (316)) *p*-tolyl chloroformate [Beil. VI-398, VI_2-(380)], b.p. 108° at 30 mm. (315) (316).]

Countless other phenols behave with $\bar{C}$ in generally similar fashion but cannot be detailed here.

With carboxylic and sulfonic acids. $\bar{C}$ with carboxylic acids or sulfonic acids or their salts at elevated temps. or in pres. of tertiary bases effects conversion to the corresponding carboxylic acid chlorides or sulfonyl chlorides.

[E.g., $\bar{C}$ with AcOH (1:1010) at 110–120° (317), or at 160° over $MgCl_2$ on diatomaceous earth (318) cf. (319) (320), or $\bar{C}$ with NaOAc at 120° under press. (321), or $\bar{C}$ with Ac_2O (1:1015) + cat. (322) gives acetyl chloride (3:7065). — $\bar{C}$ with chloroacetic acid (3:1370) over activated carbon at 200° gives (323) chloroacetyl chloride (3:5235). — $\bar{C}$ with anhydrous oxalic acid (1:0535) in pres. of tertiary amines yields (321) oxalyl (di)chloride

(3:5060). — $\bar{C}$ with cinnamic acid (1:0735) in pres. of tertiary amines yields (324) cinnamoyl chloride (3:0330). — $\bar{C}$ with phenoxyacetic acid (1:0680) in pres. of tertiary amines yields (324) phenoxyacetyl chloride (3:8790). — $\bar{C}$ with lauric acid (1:0605) at 140–150° gives (85–90% yield (325)) lauroyl chloride (3:9858). — $\bar{C}$ with palmitic acid (1:0650) at 140–150° gives (70–75% yield (325)) palmitoyl chloride (3:9912). — $\bar{C}$ with stearic acid (1:0660) at 140–150° gives (70–75% yield (325)) stearoyl chloride (3:9960). — $\bar{C}$ with oleic acid (1:0565) gives (325) oleoyl chloride (3:9940).]

[$\bar{C}$ with benzoic acid (1:0715) at 140–200° (326), or in pres. of tertiary bases or their salts (324), or $\bar{C}$ with AgOBz in s.t. at 100° (327) gives benzoyl chloride (3:6240). — $\bar{C}$ with salicylic acid (1:0780) in toluene (328) or in C_6H_6 in presence of tertiary bases (324) gives salicyloyl chloride (3:0085). — $\bar{C}$ with furoic acid (1:0475) under press. at not above 100° gives (329) furoyl chloride (3:8515).]

[Many other cases including sulfonic acids, e.g., (324), cannot be detailed here.]

With amines. *With primary amines.* $\bar{C}$ with primary amines reacts in various ways according to conditions to yield *N*-alkyl (or aryl) carbamyl chlorides, *N*-alkyl (or aryl) isocyanates, or *N*,*N'*-dialkyl (or aryl) ureas. Examples of these types of reaction are included below.

[$\bar{C}$ with $CH_3NH_2.HCl$ at 250–300° gives (285) (331) *N*-methylcarbamyl chloride [Beil. IV-64]; for stabilization of this prod. by formn. of insol. compds. with $AlCl_3$, etc., see (332); note that treatment with CaO causes loss of HCl giving (285) methyl isocyanate [Beil. IV-77, IV_1-(337), IV_2-(578)], best prepd. by other means, e.g., from NaN_3 with Ac_2O (333) or AcCl (334) (335). — $\bar{C}$ with CH_3NH_2 in C_6H_6 + aq. alkali, however, gives *N*,*N'*-dimethylurea [Beil. IV-65, IV_1-(331), IV_2-(568)], m.p. 106°.]

[$\bar{C}$ with $C_2H_5NH_2.HCl$ at 250–300° gives (285) *N*-ethylcarbamyl chloride [Beil. IV-114]; note that treatment of this prod. with CaO causes loss of HCl giving (285) ethyl isocyanate [Beil. IV-122, IV_1-(357), IV_2-(613)], b.p. 60°.]

[$\bar{C}$ with other primary aliphatic or cycloaliphatic amine hydrochlorides under conditions such that HCl is removed from reaction mixt. gives corresp. isocyanates (336) cf. (337).]

[$\bar{C}$ with aniline·hydrochloride presumably yields *N*-phenylcarbamyl chloride [Beil. XII-346, XII_1-(230)], m.p. 58–59°, but this compound is usually prepd. by other means (338) (339) since it readily loses HCl at 90–100° or by action of aq. or aq. alk. (340) giving phenyl isocyanate; for stabilization of *N*-phenylcarbamyl chloride by formn. of molecular compound with $AlCl_3$ see (332). — $\bar{C}$ *in dry aniline* (341) *or aq. aniline* (342) (96) gives *N*,*N'*-diphenylurea (carbanilide) [Beil. XII-352, XII_1-(233)], m.p. 238°; for use of this reaction as method of quant. detn. of $\bar{C}$ see (94) (95) cf. (91). — $\bar{C}$ with fused aniline HCl or carbanilide (343), or $\bar{C}$ with aniline HCl in C_6H_6 at 120° under press. (344) cf. (337), gives phenyl isocyanate [Beil. XII-437, XII_1-(259)], b.p. 166°.]

$\bar{C}$ with countless other arom. prim. amines behaves in generally similar fashion but details cannot be included here [however, for reaction of $\bar{C}$ with *p*-nitroaniline in EtOAc soln. giving *N*-*p*-nitrophenylcarbamyl chloride which on recrystn. from CCl_4 loses HCl yielding *p*-nitrophenyl isocyanate see (345) (346) (347)].

With secondary amines. [$\bar{C}$ with $(CH_3)_2NH$ in C_6H_6 at 0° (348) (349), or $\bar{C}$ over fused $(CH_3)_2NH$ HCl (350) (351), gives *N*,*N'*-dimethylcarbamyl chloride [Beil. IV-73], b.p. 167°, which with dimethylamine in C_6H_6 yields (349) *N*,*N*,*N'*,*N'*-tetramethylurea [Beil. IV-74, IV_1-(335), IV_2-(574)], liquid, b.p. 177°.]

[$\bar{C}$ with $(C_2H_5)_2NH.HCl$ at elev. temp. (350), or with $(C_2H_5)_2NH$ in C_6H_6 (352), gives *N*,*N*-diethylcarbamyl chloride [Beil. IV-120, IV_2-(611)], liquid, b.p. 186–190°, which with diethylamine gives (353) cf. (354) *N*,*N*,*N'*,*N'*-tetraethylurea [Beil. IV-120, IV_2-(611)], liquid, b.p. 210–215°.]

[$\bar{C}$ with piperidine HCl would be expected to give *N*-piperidylformyl chloride (" penta-

methylenecarbamyl chloride") [Beil. XX-54], b.p. 237–238°, but this compound has been reported only by other means.]

$\bar{C}$ with aromatic secondary amines behaves in generally analogous fashion but cannot be detailed here.

With tertiary amines. [$\bar{C}$ with *N*,*N*-dimethylaniline at ord. temp. is claimed (355) (356) to give 4,4'-*bis*-(dimethylamino)benzophenone ("Michler's ketone") [Beil. XIV-89; XIV_1-(391)], m.p. 174°. However, $\bar{C}$ passed into boilg *N*,*N*-dimethylaniline evolves CH_3Cl (3:7005) and gives (almost quant yield (357)) *N*,*N'*-dimethyl-*N*,*N'*-diphenylurea [Beil. XII-418, XII_1-(251)], m.p 121°. — Similarly, $\bar{C}$ with boilg. *N*,*N*-diethylaniline evolves C_2H_5Cl (3:7015) and gives *N*,*N'*-diethyl-*N*,*N'*-diphenylurea [Beil. XII-422], m p. 79°]

[For use of $\bar{C}$ in sepn. of a mixture of aniline, *N*-ethylaniline, and *N*,*N*-diethylaniline see (361).]

With arylhydrazines [$\bar{C}$ in toluene added to cold ether soln of phenylhydrazine gives (358) 1,5-diphenylcarbohydrazide ("diphenylcarbazide") [Beil XV-292, XV_1-(72)], m.p 175–175 5° u c. when pure (359) For use of this reaction, followed by $CuSO_4$ treatment of the resultant product, as a delicate test for $\bar{C}$ see (78).]

With other nitrogenous organic reactants [For a concise review of behavior of $\bar{C}$ with other nitrogenous classes such as amides, amidoximes, thioureas, thiosemicarbazides, etc., see the review of Dyson (360).]

With hexamethylenetetramine. $\bar{C}$ with hexamethylenetetramine in $CHCl_3$ gives (362) (363) (364) a compound of compn $\bar{C}.2C_6H_{12}N_4$, m p. 187–190° dec., (363) 196–197° from MeOH (364). — [For use of hexamethylenetetramine in paints protective against $\bar{C}$ see (365); for use of alumina or silica gels contg. hexamethylenetetramine as absorbents for $\bar{C}$ see (366)]

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3:5005 1,1-DICHLOROETHYLENE (Vinylidene (di)chloride; *unsym.*-dichloroethylene) $H_2C{=}C(Cl){-}Cl$ $C_2H_2Cl_2$ Beil. I - 186; I_1-(77); I_2-(158)

B.P. 31.7° at 760 mm. (1) F.P. −122.1° (1) D_4^{20} = 1.2129 (1) n_D^{20} = 1.4249 (1)

Care must be taken to avoid confusion of C̄ with vinyl chloride (3:7010), with 1,2-dichloroethane (ethylene (di)chloride) (3:5130), or especially with the isomeric compounds *cis*-1,2-dichloroethylene (3:5042), *trans*-1,2-dichloroethylene (3:5028), or their ordinary mixture (3:5030).

C̄ when pure is colorless liq. with mild and characteristic odor; note, however, that at temps. above 0° and especially in pres. of oxygen or other cat. C̄ polymerizes to a white powder insoluble in the monomeric C̄. (For much further comment on polymerization see below.)

PREPARATION OF C̄

[For prepn. of C̄ from 1,1,2-trichloroethane (3:5330) by elimination of 1 HCl with alc. KOH (2) (by this process C̄ was initially prepared (3)), or with excess aq. $Ca(OH)_2$ at 70–80° (90% yield (4)) (5), or with aq. or alc. NH_3 at ord. temp. (100% yield (7)), or with Na in dry ether (36) see indic. refs.; from 1,1,1-trichloroethane (3:5085) with excess aq $Ca(OH)_2$ at 70–80° see (4) (5); for formn. of C̄ (as by-product of the isomeric 1,2-dichloroethylenes (3:5030)) from trichloroethane by catalytic pyrolytic dehydrochlorination see (6).]

[For prepn. of C̄ from 1,1,1,2-tetrachloroethane (3:5555) by loss of HCl by actn. of aq. + Fe, Zn, or Cd on warming under reflux see (8); from 1-bromo-1,1,2-trichloroethane by loss of Br-Cl with Zn dust + boilg. alc. see (37).]

[For formn. of C̄ (together with vinyl chloride) from ethyl trichloroacetate (3:5950) by actn. of Zn in alc. see (9).]

[For formn. of C̄ (20% yield) from 1,2-dichloroethane (ethylene (di)chloride (3:5130) with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 400–480° see (10); note that some 22% 1,2-dichloroethylenes (3:5030) + 29% trichloroethylene (3:5170) + 29% higher chlorination prods. are also formed.]

PURIFICATION AND STABILIZATION OF MONOMERIC C̄

[For purification of C̄ by distn. as an azeotrope with MeOH, followed by removal of the latter by extraction with aq., see (11).]

Many compds. recommended as stabilizers or polymerization inhibitors for monomeric $\bar{C}$ have been described in patents: e.g., see (12) (13) (14) (15) (16).

CHEMICAL BEHAVIOR OF MONOMERIC $\bar{C}$

$\bar{C}$ + **chlorine.** [$\bar{C}$ with Cl_2 at 25–35° in pres. of absence of cat. adds 1 mole halogen giving (85–92% yield (17)) 1,1,1,2-tetrachloroethane (3:5555).]

$\bar{C}$ + **bromine.** $\bar{C}$ with Br_2 adds 1 mole halogen yielding (18) 1,1-dichloro-1,2-dibromoethane [Beil. I-93], oil, b.p. 175° at 760 mm. decg., 65° at 13 mm., f.p. −66.85°, D_4^{25} = 2.2203, D_4^{20} = 2.2449, D_4^{15} = 2.2695, n_D^{15} = 1.55930 (18).

$\bar{C}$ + **hydrogen chloride.** $\bar{C}$ with dry HCl gas at 25–35° in pres. of $AlCl_3$ or $FeCl_3$ adds 1 mole HCl giving (85–90% yields (19) (20)) 1,1,1-trichloroethane (3:5085).

$\bar{C}$ + **hydrogen bromide.** The addition to $\bar{C}$ of HBr appears to be unreported.

Polymerization of $\bar{C}$. Polymerization of $\bar{C}$ either with itself or with other cpds. (especially other substituted ethylene derivs.) leads to a large group of industrially important materials broadly designated as "vinylidene polymers" Certain plasticized and stabilized copolymer compositions have been named "Saran." [For extremely valuable comprehensive reviews of this general field see (1) (21) (22); in view of the comprehensive surveys and prior literature (including patents) references given (especially in (1)), the following text will in general include only citations since 1942.]

$\bar{C}$ when carefully purified and free from oxygen polymerizes only very slowly; however, in the pres. of various catalysts, notably peroxides, polymerization readily occurs (for amplification see (1)).

[For patents involving polymeric $\bar{C}$ from viewpoint of purification (23), storage of supercooled material (24), heat treatment to increase tensile strength (25), improvement of stability to light and heat (26) (27) (28) (29), or coloring (30) see indic. refs. — For studies on structure of fibers of polymeric $\bar{C}$ see (1) (31). — For identification of common comml. plastics (including "Saran" and "Velon") see (32).]

[For review of copolymerization of $\bar{C}$ see (1); for copolymerization with butadiene (33), with vinyl chloride or vinyl acetate (34), with styrene, acrylonitrile, various methacrylates, etc. (35), see indic. refs.]

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II 3703; *C.A.* **35**, 140 (1941). (20) I.G., Ger. 523,436, April 23, 1931; *Cent.* **1931**, I 3607; *C.A.* **25**, 3362 (1931).

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3:5010 DICHLOROACETYLENE (1,2-Dichloroethyne) Cl—C≡C—Cl C_2Cl_2 Beil. I - 245, I_1-(106), I_2-(222)

B.P.	F.P.	
32–33° at 748 mm. (1) (2) (3)	−66 to −64.2° (1)	$D_4^{20} = 1.261$ (9)
29° cor. at 743 mm. (4)		$n_D^{20} = 1.42790$ (9)

Colorless oil which ignites in air and explodes even on stirring; however, its 5–10% soln. in ether is safely handled (4).

[For prepn. of $\bar{C}$ from acetylene + aq. alk. KOCl soln. under N_2 see (1) (2) (3); from 1,1,2-trichloroethylene (3:5170) in N_2 at 130° over solid granular KOH (65% yield (4)) see (4) (5) (9); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with KOH in xylene under N_2 (can be carried out as a lect. expt.) see (6) (9); for formn. of $\bar{C}$ from barium salt of α,β,β-trichloroacrylic acid (3:1840) by htg. in H_2 see (13).]

$\bar{C}$ forms with diethyl ether a molecular cpd., $\bar{C}.C_4H_{10}O$, eas. decomposed by aq. into its components (5); for *D* and *n* of ether solns. of $\bar{C}$ see (9).

$\bar{C}$ on combustion yields CO, CO_2, $COCl_2$ (4) together with other products (5).

[For use of $\bar{C}$ in extraction of coffee see (7).]

$\bar{C}$ in CCl_4 treated 9 hrs. with strong Cl_2/CCl_4 soln. gives (1) on evapn. hexachloroethane (3:4835), m p. 187° in s.t. (1).

$\bar{C}$ on passing into Br_2/aq. yields (1) a heavy oil which on stdg. under the excess reagt. solidifies to cryst. of 1,2-dichloro-1,1,2,2-dibromoethane; after recrystn. from alc., m.p. 209–210° dec., with yellowing at 200° (1). [Note that $\bar{C}$ in CCl_4 treated with Br_2/CCl_4 can add 1 mole Br_2 giving (65% yield (4)) 1,2-dichloro-1,2-dibromoethylene, b.p. 172° at 760 mm. (8), $D_4^{15} = 2.3036$ (8), $n_D^{15} = 1.57984$ (8), m.p. +4.40° (8), 4.9° (4).]

$\bar{C}$ with I_2 in ether (4) or CCl_4 (5) gives slowly 1,2-dichloro-1,2-diiodoethylene, cryst. from ether or pet. eth., m.p. 70° (4). [Another stereoisomer, m.p. 5–7°, is formed only to extent of 10% and is removed by the solvent (5).]

[For studies on behavior of $\bar{C}$ on polymerization (10), and its reactions with NH_3 (10), amines (10) (11), alcoholates (10), diethyl sodio-malonate (10), organic Mg compds. (12), ethyl diazoacetate (12), and NO_2 (12) see indic. refs.]

3:5010 (1) Straus, Kollek, Heyn, *Ber.* **63**, 1873–1876 (1930). (2) Straus, Kollek (to I.G.), Ger. 495,787, April 17, 1930; *Cent.* **1930**, II, 1439. (3) I.G., Brit. 333, 946, Sept. 18, 1930; *Cent.* **1931**, I 523. (4) Ott, Ottenmeyer, Packendorff, *Ber.* **63**, 1941–1944 (1930). (5) Ott, Packendorff, *Ber.* **64**, 1324–1329 (1931). (6) Metz, *J. prakt. Chem.* (2) **135**, 142–144 (1932). (7)

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3:5020 METHYLENE (DI)CHLORIDE CH_2Cl_2 Beil. I - 60

(Dichloromethane) I_1-(8) *I_2-(13)*

B.P.			F.P.			
41.4–42.2°	at 760 mm.	(1)	−96.0°	(17) (10) (18)	D_4^{30} = 1.30777	(12)
41.6° cor.	at 760 mm.	(2)	−96.5°	(19) (168)		
41.5°	at 760 mm.	(3)	−96.7°	(19) (11) (20)	D_4^{25} = 1.3181	(23)
					1.31678	(12)
41.5°		(4)	−96.8°	(12) (19)	$n_D^{24.8}$ = 1.4220	(23)
41.5°	at 680 mm.	(5)	−97.0°	(21) (22)	$n_{5462}^{23.4}$ = 1.43239	(5)
41.3–41.5°		(6)			$D_{23.4}^{23.4}$ = 1.3612	(5)
40.67° cor.	at 760 mm.	(7)				
40.4°–42°		(8)			D_4^{20} = 1.3361	(15) (24)
40.1–40.3°	at 769 mm.	(9)				
40.1°	at 760 mm.	(10)			1.326	(25)
40.0°		(11)			1.32578	(12)
39.95°	at 760 mm.	*(12)*			n_D^{20} = 1.4253	(25)
39.93–40.12° cor.		(13)			1.4249	(13)
39.9	at 736 mm.	(14)			1.4237	(26)
39.8°	at 760 mm.	(15)			1.4234	(15)
39.5–40.1°		(16)			D_4^{15} = 1.33479	(12)
					$n_{He(yellow)}^{15}$ = 1.42721	(12)
					D_4^0 = 1.3620	(23)
					n_D^0 = 1.4361	(23)

Note 1. For study of vap. press. of C̄ over range −87° to +38° see (7).

Note 2. For influence of very high press. on f.p. of C̄ see (20).

For D_4^t over range t = −100° to +40° see (25); −273 to −194° see (10).

MISCELLANEOUS PHYSICAL PROPERTIES OF C̄

Various Solubility Relations

With water. C̄ is only slightly soluble in aq. and readily volatile with steam. E.g., 100 g water dissolves following amts. of C̄: 2.363 g. at 0° (27), 2.122 g. at 10° (27), 2.000 g. at 20° (27) (15), 1.969 g. at 30° (27). — *For study of soly. of water in C̄ at 0°, 25°, and 30°* see (28) (29); for study of reciprocal soly. of C̄ and water see (30) (68). — C̄ with H_2O is claimed (35) to form a hydrate stable up to +2°.

With organic compounds. [For studies on soly. of C̄ in 35 org. solvents of various types see (31); for soly. of C̄ in cellosolve acetate (33), carbitol acetate (32) (33), diethylene glycol diethyl ether (32), tetraethylene glycol dimethyl ether (32), and tetraethylene glycol diethyl ether (33) see indic. refs]

Binary Systems Containing $\bar{C}$

(See also azeotropes containing $\bar{C}$)

$\bar{C}$ + Cl_2: for f.p./compn. data and diagram (various compounds and eutectics are formed) see (21).

$\bar{C}$ + C_2H_5Cl (*3:7015*): for f.p./compn. data and diag (eutectic, f.p. −149.7°, conts. 31.7 wt. % $\bar{C}$) see (17). — $\bar{C}$ + $CHCl_3$ (*3:5050*): for f.p./compn. data and diag. (eutectic, f.p. −108 4°, conts. 70 5 wt. % $\bar{C}$) see (17); for data on b.p., D_4^{20}, and liq./vapor equilibria see (34). — $\bar{C}$ + CCl_4 (*3:5100*): for data on b.p., D_4^{20}, and liq./vapor equilibria see (34). — $\bar{C}$ + 1,1,-*dichloroethane* (*3:5035*): for f.p./compn. data see (19). — $\bar{C}$ + 2,2-*dichloropropane* (*3:7140*): for f.p./compn. data see (22).

$\bar{C}$ + *isobutyl bromide:* for f.p./compn. data see (19). — $\bar{C}$ + *methylene (di)bromide:* for f.p /compn data see (19)

$\bar{C}$ + *methylene (di)iodide:* for f.p./compn. data see (19).

$\bar{C}$ + *dimethylaniline:* for D_4^{25} and $n_D^{24.8}$ for 0–100% $\bar{C}$ *see* (23); for f.p./compn. data and diagram (eutectic, m.p. −97.2°, conts. 91 wt. % $\bar{C}$) see (168).

Ternary Systems Containing $\bar{C}$

(See also azeotropes containing $\bar{C}$)

$\bar{C}$ + $CHCl_3$ + CCl_4: system forms ternary eutectic, f.p. −111.4°, contg. 60 wt. % $\bar{C}$ + 27.0 wt. % $CHCl_3$ (3:5050) + 13 0 wt. % CCl_4 (3:5100) (17).

Binary Azeotropes Containing $\bar{C}$

$\bar{C}$ + H_2O: $\bar{C}$ forms with aq. a const -boilg. mixt., b.p. 38.1°, contg. 98.5 wt. % $\bar{C}$ (68).

$\bar{C}$ + *MeOH:* $\bar{C}$ forms with MeOH (1:6120) a const.-boilg. mixt., b.p. 39.2° (4) at 760 mm (3), contg. 92 wt. % (3), 94 wt. % (4) $\bar{C}$. — $\bar{C}$ + *EtOH:* $\bar{C}$ forms with EtOH (1:6130) a const.-boilg. mixt., b.p. 41.0° at 760 mm. (3), contg. 96.5 wt. % (3) $\bar{C}$. — $\bar{C}$ forms with formaldehyde dimethylacetal (1:0105) a const -boilg. mixt., b.p. 45.0° (36), contg. (36) 41 wt. % $\bar{C}$, cf. (37). — $\bar{C}$ + *acetone:* note that this system forms no azeotrope; note also *that* $\bar{C}$ *is the only known liquid which with* MeOH (see above) gives a const.-boilg. mixt boilg. lower than acetone and at the same time not forming a binary azeotrope with acetone (4).

Ternary Azeotropes Containing $\bar{C}$

$\bar{C}$ + H_2O + *EtOH:* forms no ternary azeotrope (68).

$\bar{C}$ + *MeOH* + *acetone:* this system forms no ternary azeotrope; for discussion see (4) (38).

$\bar{C}$ + $CHCl_3$ + *acetone:* for discussion see (4).

Other Physical Properties of $\bar{C}$

[For study of thermal conductivity of $\bar{C}$ see (39); for studies of heat capacity of $\bar{C}$ (40) as calculated from spectroscopic data (41) see indic. refs.; for studies of critical temp. of $\bar{C}$ (7) (15) (6) and method for its microdetermination (6) see indic. refs.; for ebullioscopic const , viz., 2.6° for 1000 g. $\bar{C}$, see (43).]

[For studies of adsorption of $\bar{C}$ on wood charcoal at 25° and 50° (44) or on cocoanut charcoal over range −31.5° to 184° (45), on $Al(OH)_3$ gel (46), on $Fe(OH)_3$ gel (47), on Cr_2O_3 (48) see indic. refs ; $\bar{C}$ is preferentially adsorbed (42) by silica gel from its mixt. with $CHCl_3$ (3:5050).]

[For study of attempt to separate isotopes of Cl_2 by reversible fractional distn. of $\bar{C}$ see (49).]

PHYSIOLOGICAL ASPECTS OF $\bar{C}$

$\bar{C}$ has low toxicity compared to other chlorinated hydrocarbon solvents; the maximum allowable conc. for 8 hrs. daily exposure is 500 p p m. (50). [For study of relative toxicity of $\bar{C}$ see (51); for extensive study of industrial hygiene and toxicity of $\bar{C}$ (together with 12 other chlorinated solvents (52)) (53) (50) see indic. refs.; for study of $\bar{C}$ upon running activity of male rat see (54).]

USES OF $\bar{C}$

$\bar{C}$ is widely used as a solvent, as a fluid for refrigeration processes, and for removing water from other organic materials; examples of all these aspects are cited below.

[For study of utility of $\bar{C}$ as solvent for the ozonization of org. compds. see (10); for use of $\bar{C}$ as solvent for the extraction of vitamin A (55) or of soy-bean oil (56) see indic. refs.; for general studies (15) (57) (58) and patents (59) (60) (61) (62) (63) (64) (65) on use of $\bar{C}$ in refrigerating machines and systems see indic. refs.; for use of $\bar{C}$ in detn. of water content of liquids (66) (67) or for prepn. of abs. EtOH (68) (69) (70) see indic. refs.]

DETECTION OR DETERMINATION OF $\bar{C}$

[For detection of $\bar{C}$ in pres. of acetone (by means of Fujiwara color test with pyridine + NaOH) see (71); for distinction of $\bar{C}$ from $CHCl_3$ (3:5050) and from CCl_4 (3:5100) by color tests see (72) (73) (also under ⓑ below).]

[For detn of $\bar{C}$ in blood by removal through aeration, pyrolytic decompn. of $\bar{C}$, and alk. absorption of resultant HCl as directed see (74); for detn. of C, H, and Cl in $\bar{C}$ by combustion see (75). Note that the R. + H. Tri-Per Analyzer, a recording ultra-violet photometer very useful for detn. of trichloroethylene (3:5170) and tetrachloroethylene (3:5460), is insensitive (76) to $\bar{C}$.]

PREPARATION OR FORMATION OF $\bar{C}$

From methane. [The chlorination of CH_4 under various conditions to yield $\bar{C}$ (accompanied by more or less CH_3Cl (3:7005), $CHCl_3$ (3.5050), and CCl_4 (3:5100)) has been extensively studied and no attempt will be made here to sift out details. For examples of leading scientific papers ((77)–(88), incl.) and patents ((89)–(96), incl.) see indic. refs.]

From methyl chloride. [The chlorination of MeCl to $\bar{C}$ has also been extensively studied; many of the relevant data are included in the papers and patents on the chlorination of methane (see preceding paragraph), to which should be added the following patents (91) (97) (98) (99) (100). Note patent (98) on separation of MeCl (3:7005) from $\bar{C}$ by hydrolysis of former to MeOH (1:6120) with $Ca(OH)_2$ under press.]

From chloroform. [For formn. of $\bar{C}$ from $CHCl_3$ (3:5050) by replacement of 1 chlorine by hydrogen using Zn + alc. HCl (101), Zn + AcOH (103), Zn dust + alc. NH_3 (102) (8) (2), Al/Hg + aq. (103), Fe + AcOH (103), or Si_3H_8 + $AlCl_3$ in absence of air (104) see indic. refs]

From carbon tetrachloride. [For prepn. of $\bar{C}$ from CCl_4 (3:5100) using aq. $FeSO_4$ + NaOH see (105).]

From miscellaneous sources. [For prepn. or formn. of $\bar{C}$ from CH_2I_2 with Cl_2 (first prepn. of $\bar{C}$) (106) cf. (158); from polyoxymethylene with PCl_5 in s t. (107); from MeOH + S_2Cl_2 + Cl_2 (108); or from chloroacetic acid (3:1370) by electrochem. oxidn. (109) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Oxidation of $\bar{C}$. [$\bar{C}$ with air at ord. temps. and press. does not give inflammable mixts.; at high temps. vapor of $\bar{C}$ becomes inflammable and ignites at 642° in air, at 606° in O_2;

limiting concns. of C̄ for inflammability in O_2 are 15.5–66.4%; N_2 does not greatly affect the lower limit of inflammability in O_2 but greatly reduces the upper limit (110). — For study of inflammability of mixts. of C̄ with $O_2 + N_2$, air + CO, or $O_2 + N_2$ + MeBr see (111). — For effect of C̄ on flash point of solvents see (115).]

[C̄ with atomic O gives (112) $COCl_2$ (3:5000), Cl_2, HCl, $CO_2 + H_2O$; C̄ with air over CuO at 450° gives (113) little $COCl_2$ (3:5000); for study of Cl_2-sensitized photochem. oxidn. of C̄ see (114).]

Fluorination of C̄. [C̄ with SbF_3 + cat. readily gives (126) (127) CH_2F_2, b.p. −51.6°, + CH_2ClF, b.p. −9.0°.]

Chlorination of C̄. [C̄ with Cl_2 as directed (116) (117), or C̄ with HCl gas + air over $CuCl_2$ at 440° (118), gives $CHCl_3$ (3:5050) and CCl_4 (3:5100).]

Bromination of C̄. [C̄ with Br_2 cf. (158) in pres. of Al gives (128) cf. (129) CH_2BrCl + CH_2Br_2 [Beil. I-67, I_1-(16), I_2-(32)], b.p. 96.95° at 760 mm., f.p. −52.7°, D_4^{25} = 2.48417, D_4^{20} = 2.49702 (130). — For an alternative synthesis of CH_2Br_2 (88–90% yield) from *$CHBr_3$ with Na_3AsO_3 + NaOH see (138).*]

Hydrolysis of C̄. C̄ on suitable hydrolysis yields formaldehyde (1:0145). [E.g., C̄ with aq. in pres. of weakly alk. reacting salts such as $NaHCO_3$, Na_2HPO_4, NaOAc, etc., at 165° under press. (119), or C̄ + N_2 over dry Na_2CO_3 at 310–320° (120), C̄ with steam over activated carbon at 260–270° (121), C̄ with aq. at 140–170° under press. (122), C̄ with steam at 550–850° over cat. (123), or C̄ with steam over tin phosphate at 460° (124) gives formaldehyde (1:0145) + HCl. Note that C̄ on protracted htg. with aq. at 180° gives (125) formic acid (1:1005), MeCl (3:7005), MeOH (1:6120) HCl + CO.]

Behavior with inorganic salts. [C̄ with NaI in acetone htd. in press. bottle for 20 hrs. as directed (131), or C̄ with NaI in acetone, MeOH, or EtOH at 120–130° under press. (132), gives (60% yield (131)) methylene (di)iodide [Beil. I-71, I_1-(18), I_2-(37)], b.p. 151–153° cor. at 330 mm. (133), 88° at 39 mm. (134), 66–67° at 11–12 mm. (24); exists in two crystn. forms, stable form, m.p. + 5.85° (135), metastable form, m.p. 40° (136); D_4^{25} = 3.3078 (130); D_4^{20} = 3.3212 (130); D_4^{15} = 3.3345 (130); n_D^{15} = 1.74428 (130). — For an alternative synthesis of CH_2I_2 (90–97% yield) from iodoform by treatment with Na_3AsO_3 + NaOH see (137).]

[C̄ with 2 moles K_2SO_3 in aq. at 150–1[illegible] potassium salt of methanedisulfonic acid ([illegible]

[C̄ with alc. $AgNO_3$ does *not* react even [illegible] $CHCl_3$ (3:5050) nor CCl_4 (3:5100) reacts either, CH_3Cl (3:7005) gives a ppt. within 3 hrs. (140).]

[For formn. of polymeric prods. from reaction of C̄ with metal sulfides or polysulfides see (141); for study of photochem. reaction of C̄ with H_2S see (149).]

Behavior with metals. C̄ (like many other polyhalogenated hydrocarbons) in presence of metallic K, Na, K/Na alloy, or even of certain other active metals explodes under the influence of mechanical or thermal shock. [For study of this characteristic (142), especially with regard to sensitivity toward Li, Na, K, Ca, Sr, Ba (143), see indic. refs.]

[Note that C̄ with molten sodium at 200–300° gives (144) C, H, and CH_4, together with smaller amts. of ethane, ethylene, and acetyle[illegible] of H_2 gives (145) 92% CH_4 + 8% ethylene, while C̄ [illegible] ethylene; for further studies of behavior of C̄ [illegible] attempts to obtain a free methylene radical (CH_2) with C̄ + Na vapor have been unsuccessful (148).]

[For study of stability of various metals with respect to corrosion by C̄ under various conditions see (15).]

Behavior with various organic reactants. [$\bar{C}$ with CO + $AlCl_3$ at 260° and 800 atm. press. for 8 hrs. gives (150) chloroacetyl chloride (3:5235); but $\bar{C}$ with CO, COS, or $COCl_2$ (3:5000) + cat. at 700° gives (151) malonyl (di)chloride (3:9030).]

[$\bar{C}$ with C_6H_6 + $AlCl_3$ gives (152) cf. (153) diphenylmethane (1:7120); $\bar{C}$ with toluene + $AlCl_3$ gives (152) di-*p*-tolylmethane [Beil. V-615, V_1-(289), V_2-(518)], m.p. 28° (154), b.p. 302° cor. at 768 mm (154), accompanied by considerable (152) (155) 2,7-dimethylanthracene, m.p. 241° cor. (155), $\bar{C}$ with *o*-xylene (1:7430) + $AlCl_3$ in acetylene tetrachloride (3·5750) as solvent gives (156) 2,3,6,7-tetramethylanthracene, m.p. 299° (156); for behavior of $\bar{C}$ in pres. of $AlCl_3$ with *m*-xylene (1.7420) or with pseudocumene (1:7470) see (152).]

[$\bar{C}$ with CH_2Br_2 + 5–10% KCl in pres. of moistened $AlCl_3$ at 180° in s.t. for 16 hrs. undergoes a redistribution reaction giving (157) a mixt. contg 33% $\bar{C}$ + 18% CH_2Br_2 + 50% $ClCH_2Br$; $\bar{C}$ with CH_2I_2 similarly treated at 114° for 18 hrs. gives (157) a mixt. contg. 33% $\bar{C}$ + 21% CH_2I_2 + 46% $ClCH_2I$.]

[$\bar{C}$ with NaOMe in s.t. at 100° (158), or vapor of $\bar{C}$ over NaOMe + pumice at 200° (37), gives formaldehyde dimethylacetal (1:0105); $\bar{C}$ + NaOEt in s.t. at 100° (158), or $\bar{C}$ with excess EtOH + calcd amt. NaOH at 100–125° under press. (159), gives formaldehyde diethylacetal (1:0135); for analogous behavior of other alcoholates (158) (159) or phenolates (158) see indic. refs.]

[$\bar{C}$ with alc. NH_3 at 125° in s.t. gives (160) hexamethylenetetramine [Beil. I-583, I_1-(306)]. — $\bar{C}$ with Me_2NH in s.t. at 70° gives (161) *bis*-(dimethylamino)methane. — $\bar{C}$ with Me_3N in 90% acetone at 55° or more slowly in ether undergoes a quaternization reaction giving trimethyl-chloromethyl-ammonium chloride (constants not detd) (162).]

Ⓟ **Beilstein test for halogen.** Note that because of its low b.p. $\bar{C}$ often appears to fail in Beilstein copper gauze test for halogen compds.; in such cases use the modification described by (163) (164)

Ⓟ **Hydrolysis to formaldehyde.** $\bar{C}$ (2 g.) in 10% MeOH/alk. (20 ml.) boiled 20 min. under good reflux, subsequently acidified with dil. H_2SO_4, gives soln. containg. Cl^- and formaldehyde (1:0145).

Ⓟ **Color reaction with α-naphthol/cyclohexanol.** $\bar{C}$ (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (72) blue color; one portion of this blue soln. underlaid with equal volume 85% H_2SO_4, stood 1 minute and shaken, turns green-blue; a second portion of the alkaline blue soln. acidified with equal volume of AcOH (1:1010) stood 1 minute and shaken becomes yellow. [Note that the alkaline boiling also gives a blue color with $CHCl_3$ (3:5050) and with CCl_4 (3.5100) while other chlorinated solvents (72) give yellow-brown, gray, or brown; in the H_2SO_4 acidification both $CHCl_3$ and CCl_4 give blue rather than green-blue; in the AcOH acidification $CHCl_3$ gives an orange-yellow, CCl_4 a red color]

Ⓟ **Color test with 2,7-dihydroxynaphthalene/cyclohexanol.** $\bar{C}$ (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives steel-blue color (73) [Note that under these conditions $CHCl_3$ (3:5050) gives a deep-red color while CCl_4 (3 5100) gives a pale yellow brown.]

Ⓟ **Color test with cyclopentanol.** $\bar{C}$ (1 drop) in cyclopentanol (1 ml.) with 1 pellet NaOH boiled 25 seconds, then shaken vigorously for 35 seconds, gives deep red color; upon addition of 4 ml. 96% EtOH and shaking color intensifies or becomes reddish brown (73). [Note that after addn. of alc. $CHCl_3$ gives only a pale citron-yellow or

yellowish brown and that as little as 20% of C̄ can be detected by this means in $CHCl_3$ (73); CCl_4 gives (73) after addn. of alc. an intense nut-brown.]

—— Formaldehyde di-α-naphthylacetal (methylene di-α-naphthyl ether): unreported.

Ⓓ Formaldehyde di-β-naphthylacetal (methylene di-β-naphthyl ether): m.p. 134° (165), 133–134° (166). [From CH_2I_2 with Na β-naphtholate refluxed in alc. (165) (166) (167); not actually reported from C̄ but presumably resulting by above method if some KI be added to refluxing mixture of C̄ + Na β-naphtholate in acetone. Note that this ether fails (165) (167) to form any PkOH addition compound.]

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3:5025 1,1,3-TRICHLORO-2-METHYLPROPENE-1 $C_4H_5Cl_3$ Beil. S.N. 11

$$\begin{array}{c} \qquad\quad CH_3 \\ \qquad\quad | \\ ClCH_2—C{=}CCl_2 \end{array}$$

B.P. 45–46° (1)

Note: C̄ readily undergoes allyl transposition so that in reactions of C̄ products derived from the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) may be expected (1) (2) (3)

[For prepn. of C̄ (57% yield (1)) from β,β,β-trichloro-*ter*-butyl alc. ("Chloretone") (3:2662) by htg. to 200° with P_2O_5 and dimethylaniline see (1).] [A 15% yield of the isomeric 1,1,1-trichloro-2-methylpropene-2 (3:5605) together with some α-chloroisobutyric acid (3:0235) are separated from C̄ by redistillation (1).]

C̄ on hydrolysis by boilg. 2 days with AgOH at 100° under pressure gives (22% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, b.p. 78–79°, $D^{20}_{-} = 1.298$, $n^{20}_{-} = 1.493$. [The corresp. ether, b.p. 129° at 11 mm., $D^{20}_{-} = 1.330$, $n^{20}_{-} = 1.5108$, is also formed in 22%

yield (2).] The alc may be characterized by its *p*-nitrobenzoate, m.p. 91°, or its *N*-phenylcarbamate, m.p. 64° (2).

Č on htg. with NaOAc + AcOH gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm., D_-^{20} = 1.257, n_-^{20} = 1.4718 (2). [With boilg. NaOH this ester regenerates the corresp. alc. (2).]

Č with NaOEt gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, b.p. 56° at 12 mm., D_-^{20} = 1.1285, n_-^{20} = 1.4610 (2).

Č in $CHCl_3$, treated with O_3, then hydrolyzed gives α-chloroacetone (3:5425), b.p. 60–62° at 50 mm (1).

[For reactns. of Č with CaI_2 and with CH_3MgBr see (2).]

- ⓓ 1,1,1,2,3-Pentachloro-2-methylpropane (3:1265): m.p. 59.5° (2). [From Č by direct treatment with Cl_2 (2).]
- ⓓ 1,2-Dibromo-1,1,3-trichloro-2-methylpropane: m.p. 108° (2). [From Č on warming 1 day with excess Br_2, then distg. at 12 mm. (2).]
- ⓓ 3,3-Dichloro-2-methylpropen-2-yl *p*-nitrobenzoate: m.p. 91° (2). [From Č on boilg. with dil. alc. soln. of K *p*-nitrobenzoate (2).]

3:5025 (1) Jacob, *Bull. soc. chim.* (5) 7, 581–586 (1940). (2) Kirrmann, Jacob, *Bull. soc. chim.* (5) 7, 586–593 (1940). (3) Kirrmann, Jacob, *Compt. rend.* 203, 1528–1529 (1936).

3:5028 *trans*-1,2-DICHLOROETHYLENE (*trans*-Acetylene dichloride)

Cl—C—H
  ‖
H—C—Cl

$C_2H_2Cl_2$ Beil. I — I_1-(78) I_2-(150)

B.P.		F.P.	
[18.8–50.2° (35)]		−53.1° (34)	D_4^{25} = 1.2480 (1)
48.8° at 763 mm. (1)		−53.0° (12)	n_D^{25} = 1.43060 (7)
48.1–49.4° at 741 mm. (2)		−50.0° (13)	D_4^{20} = 1.2560 (1)
48.35° at 760 mm. (3) (4) (13)			
48.3° at 760 mm. (5)			n_D^{15} = 1.44602 (6)
48.2–48.4° at 769 mm. (6)			
47.85–47.87° at 759.5 mm. (7)			D_4^{15} = 1.2631 (3)
47.5° (8)			1.2650 (4)
47.48° (9)			n_D^{15} = 1.44903 (3)
47.3° (10)			
47.2° at 745 mm. (11)			
48.20–47.87° at 759.5 mm. (27)			

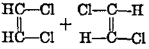
See also both *cis*-1,2-dichloroethylene (3:5042) and ordinary (mixt. of *cis* and *trans*) 1,2-dichloroethylene (3:5050); *the following text is restricted to studies on substantially pure trans stereoisomer.*

Note carefully that 1,2-dichloroethylene is not the same as ethylene (di)chloride (3:5130) (*there are an almost incredible number of errors in the literature involving this point*); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene (di)-chloride) (3:5[illegible]5).

GENERAL DATA ON Č

Note that substantially pure Č is a commercial solvent in U.S.A. under designation "Di 45" (referring to the two chlorine atoms and the b.p.). [*For study of thermal conductivity and for tabulation of constants of commercial* Č *see* (14). — *For toxicity of* Č *see* (26) (15). — *For use of* Č *in extraction of caffeine from coffee see* (16).]

3:5030 1,2-DICHLOROETHYLENE (Acetylene dichloride) } ord. mixt. $C_2H_2Cl_2$ Beil. I - 187, I_1-(77), I_2-(158)



cis (3:5042) *trans* (3:5028)

The text under this heading refers to the ordinary mixt. of the two individual stereoisomeric forms, viz., *cis*-1,2-dichloroethylene (3:5042) and *trans*-1,2-dichloroethylene (3:5028). Since the proportion of the two stereoisomers differs according to conditions and previous treatment no definite physical constants can be given, and those for each pure stereoisomer should be consulted.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); *neither is it the same as 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005).*

Furthermore note that some confusion exists in the literature on the relationship between the two isomers; the high-boilg. stereoisomer (3:5042) is now definitely regarded as the *cis* form and the lower-boilg. stereoisomer (3:5028) as the *trans*; however, some records (including "International Critical Tables") have inverted these designations.

PHYSICAL DATA ON C̄

General. Ordinary comml. C̄ consists of a mixt. of the two stereoisomers; by careful fractional distn. the two stereoisomers can be separated (for references see text of the two pure stereoisomers). — *An equilibrium mixt. contg. about 20% of the lower-boilg. (trans)* (3:5028) and 80% of the higher-boilg. (*cis*) (3:5042) forms can be obtd. from either by treatment at ord. temp. in sunlight with 1–2% Br_2 (for data on thermal isomerization see text of both individual stereoisomers). — Note also that the two pure stereoisomers (q.v.) form a eutectic, f.p. −91°, contg. about 29% *trans* + 71% *cis* forms.

Solubility relationships of C̄. Soly. of C̄ in aq. is 0.8 ml. per 100 ml. aq. at ord. temp. (1). — [For soly. of I_2 in C̄ over range 11–25° (2) and use of such solns. in detn. I_2 number of oils and fats (3) (4) see indic. refs. — For solv. power of C̄ for various org. cpds. see (5) (6).]

Inflammability of C̄. C̄ with air forms explosive mixt. in range contg. 3.3–15.3% C̄ (7); 9.7–12.8% C̄ (8). [For studies of influence of vapors of C̄ on mixts. of air with CH_4 (8), acetylene (10), CO (10) (12), or H_2 (10) see indic. refs.]

Miscellaneous data. [Ebullioscopic const. of C̄ (for 1 mole solute in 100 g. C̄) = 29.6 (14).]

USES OF C̄

[For use of C̄ as solv. for fats and oils (15), as refrigerating liquids (16) (17) (18) (19) (20) (21), for extraction of caffeine from coffee (22), for dehydration (concentration) of propionic acid from aq. solns. (23), for sepn. of *o*- and *p*-isomers of various phenols (24), in dewaxing of mineral lubricating oils (25), for pretreatment in dyeing of cellulose esters and ethers (26) see indic. refs.]

PHYSIOLOGICAL BEHAVIOR OF C̄

C̄ acts as an anesthetic and narcotic, but full treatment of this aspect is beyond the scope of this work; for lead references, however, see below.

Toxicity of C̄. [For studies on toxicity of C̄ see (27) (28) (29) (30) (31); for studies of narcotic action (31) (33) (34) (35) (36) see indic. refs.]

Antiseptic and disinfectant props. of Č. [For studies of Č from this viewpoint see (37) (38) (1).]

DETERMINATION OF Č

Č is detd. by conversion of its halogen by pyrolytic or by chem. means completely to chloride ion followed by either volumetric or gravimetric detn. of the latter.

[For detn. of Č by methods involving *pyrolytic decompn. of* Č see (39) (40) cf. (41).]

[For detn. of Č by methods involving decompn. of Č with Na + ethanolamine in dioxane see (42) cf (43).]

[For detn. of Č by means of $HgSO_4$ catalyzed addn. of Br_2 (from bromide/bromate soln.) to its unsatd. linkage see (44).]

PREPARATION OF Č

From various polychloroethanes. *From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).* [For prepn. of Č from acetylene tetrachloride by removal of 2 chlorine atoms with H_2 over Ni at 300–320° (45), with Fe or Al + aq. (46) (47) or Zn + aq. (47) (48), with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq vapor (50), or by electrolytic reduction in pres of $ZnCl_2$ (51) cf (52) see indic refs. — Note that Č is also one of the prods. of *pyrolysis* of acetylene tetrachloride over pumice at 700° (53).]

From 1,1,1,2-tetrachloroethane (3:5555). [For prepn. of Č from *unsym.*-tetrachloroethane with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (49) preferably in pres. of aq. vapor (50) see indic. refs.; note that mechanism yielding this result is unknown.]

From 1,1,2-trichloroethane (3:5330). [For prepn. of Č from 1,1,2-trichloroethane (by loss of HCl) over $CuCl_2$ on pumice at 400° (54) or with MeOH over Al_2O_3 at 290° (MeCl (3:7005) is also formed) (55) see indic. refs]

From 1,2-dichloroethane (3:5130). [For formn. of Č (22% yield) together with other prods. from ethylene (di)chloride with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 400–480° see (56).]

From various mixed-halogenated ethanes. [For formn. of Č from 1,2-dibromo-1,2-dichloroethane (Beil. I-93, I_1-(29), I_2-(64)] by removal of 2 Br with Zn in alc. (57) or with H_2 over Ni at 300–320° (45) see indic. refs.; from 2-bromo-1,1,2-trichloroethane (by elimination of Br-Cl) with Zn dust in boilg. alc. (58) (59) or from 2-iodo-1,1,2-trichloroethane on distn. at atm. press. (60) see indic. refs.]

From acetylene. *With chlorine.* [Starting from acetylene the addition of 1 mole of Cl_2 yields Č to which further addn. of Cl_2 gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3.5750), for this reason most of the processes for prepn. of the latter cpd. by this method yield (or may be made to yield) Č as a by-product. Since the patents on the addn. of chlorine to acetylene have been extensively cited under the text of 1,1,2,2-tetrachloroethane (3:5750) (prepn. from acetylene), refer to that compound; however, see also (61) (62) (63)]

With other reagents. [For formn. of Č from acetylene with $SbCl_5$ (64) (65) cf. (57), with $SbCl_5 + SbCl_3$ (66), or with aq. ICl soln. (57), see indic. refs.]

CHEMICAL BEHAVIOR OF Č

Pyrolysis of Č. [Č *in s.t. at 360° for 10 hrs. is completely decomposed* (64) into carbon + HCl.] (See also above under detn. of Č.)

Oxidation of Č. [Č with O_2 in pres. of suitable cat. (e.g., Br_2 or H_2SO_4) gives (67)

chloroacetyl chloride (3:5235). — $\bar{C}$ with O_2 + N_2 in ultra-violet light evolves HCl but yields (68) only resinous (perhaps polymerization) products.]

[For study of rate of reactn. of $\bar{C}$ (in AcOH) with O_3 see (69).]

[Note that $\bar{C}$ with NH_3 + air over Pt/Rh cat. at 820–850° gives (70) HCN.]

[$\bar{C}$ with air over (strongly chlorinated) CuO at 450° gives (76) much phosgene (3:5000).]

Stabilization of $\bar{C}$. [For stabilization of $\bar{C}$ by addn. of small amts. of alc. NH_3 (71), with Et_3N (72), or with various phenols, amines, and aminophenols (73), see indic. refs.] (See also under corresp. subtopic of 1,1,2-trichloroethylene (3:5170).)

Polymerization of $\bar{C}$. [$\bar{C}$ in the pres. of dibenzoyl peroxide (or other org. peroxides) on htg. under press. reacts with itself yielding mainly (74) a dimer, viz., 1,3,4,4-tetrachlorobutene-1 (3:9058), accompanied by other prods.]

[For study of influence of radiation of 1980–1860 Å (from Al arc) and accompanying polymerization see (75).]

Reaction with halogens. *Behavior of $\bar{C}$ with Cl_2.* [$\bar{C}$ adds 1 mole Cl_2 giving (69% yield (58)) 1,1,2,2-tetrachloroethane (3:5750); for study of this reactn. in light of 4360 Å see (77).] (See also under the individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers)

Behavior with Br_2. [$\bar{C}$ adds 1 mole Br_2 giving (60) (57) 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I_1-(29), I_2-(64)], b.p. 195° at 760 mm. (78) (59), b.p. 79.0–79.5° at 15 mm. (79); for study of photochem. addn. of Br_2 in gas phase (80) (81) and in CCl_4 soln. (81) (82) in sunlight (83) (84) see indic. refs.]

Behavior with ICl. [$\bar{C}$ in $CHCl_3$ adds ICl in sunlight yielding (60) 2-iodo-1,1,2-trichloroethane, b.p. 77° at 9 mm., D_4^{15} = 2.2760 (60).]

Reaction with halogen hydrides. *Reaction with HCl.* [$\bar{C}$ in the absence of cat. does not add dry HCl; $\bar{C}$ with dry HCl in the pres. of small amts. $AlCl_3$ at 30–40° gives (87% yield (86)) (85) (104) 1,1,2-trichloroethane (3:5330) accompanied (85) by 1,1,2,3,4-pentachlorobutane (3:0750); this latter prod. and doubtless various others appear to be formed in the pres. of the $AlCl_3$ by various condensations among the various organic materials (see below).]

Reaction with H_2SO_4. [$\bar{C}$ is only slightly attacked at 20° by either 85% or 96% H_2SO_4 and no polymerization occurs (87); on running the H_2SO_4 layer into 10 vols. of cold aq. qual. evidence of formn. of chloroacetaldehyde (3:7212) was obtd. (87). — $\bar{C}$ with conc. H_2SO_4 is unchanged up to 120° but at higher temps. carbonizes without evidence of formn. of chloroacetaldehyde (88).]

[However, $\bar{C}$ with fuming H_2SO_4 (50% SO_3) or $\bar{C}$ with SO_3 followed by aq. gives (88) (89) chloroacetaldehydesulfonic acid from which htg. with 80% H_2SO_4 gives (88) (89) chloroacetaldehyde (3:7212).]

Behavior with alkali. [$\bar{C}$ with alc. KOH (90) (91) loses 1 HCl yielding chloroacetylene (3:7000); this prod. sometimes (92) (93) causes spontaneous ignition of the system especially when its alc. soln. comes in contact with air in cleaning the reaction flask (91).] (See also under the individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers.)

[Note that $\bar{C}$ with alc. NaSH does *not* react even after 6 hrs. reflux. (92).]

Behavior with NH_3. [$\bar{C}$ with liq. NH_3 under high press. reacts only very slightly although a small amt. of chloroacetylene (3:7000) (from loss of HCl) is formed (94).]

Behavior with metals. [For study of corrosion of common metals by $\bar{C}$ see (5).]

Behavior with other inorganic reactants. [$\bar{C}$ with liq. nitryl chloride ($ClNO_2$) in s.t. at 100° for 3 hrs. gives by addn. to unsatd. linkage (67% yield (95)) 2-nitro-1,1,2-trichloroethane, pale yel. oil, b.p. 63° at 13 mm. — $\bar{C}$ cautiously added to 4 vols. of a mixt. of conc. + fumg. HNO_3 and warmed gives (96) a small amt. of nitro-trichloromethane (chloropicrin).— $\bar{C}$ with liq. N_2O_4 at ord. temp. for 24 hrs. in an *unsealed* tube (use of sealed tube leads to serious explosions) reacts (96) to give a little oxalic acid dihydrate (1:0445) together with an unidentified lachrymatory oil.]

BEHAVIOR WITH ORGANIC REACTANTS

With hydrocarbons. [$\bar{C}$ (1 mole) with cyclopentadiene (1 mole) (1:8030) in s.t. at 180–190° for 15 hrs. yields (97) two Diels-Alder type adducts. — For reactn. of $\bar{C}$ with C_6H_6 + Al/Hg see under individual *cis*- (3:5042) and *trans*- (3:5028) stereoisomers.]

With other chlorinated hydrocarbons. (For reaction of $\bar{C}$ with itself see above under polymerization.)

With methylene (di)chloride (3:5020). [$\bar{C}$ (1 wt. pt.) with CH_2Cl_2 (3 wt. pts.) + $AlCl_3$ (0.3 wt. pt.) at 40° for 8 hrs. gives (24% yield (98)) 1,1,2,3-tetrachloropropane (3:6035)].

With chloroform (3:5050). [$\bar{C}$ (1 wt. pt.) with $CHCl_3$ (3 wt. pts.) + $AlCl_3$ (0.25 wt. pt.) stirred with sand for 20 hrs. at 30° (99) cf. (100) (101) (102) gives (yields: 63% (99), 70–75% at 50° (100), 46% at 17° in 22 hrs. (100)) 1,1,2,3,3-pentachloropropane (3:6280).]

With carbon tetrachloride (3:5100). [$\bar{C}$ with CCl_4 + $AlCl_3$ gives (101) (102) cf. (103) 1,1,1,2,3,3-hexachloropropane (3:6460); for reactn. of this system yielding heptachloropentenes see (103).]

With 1,1,2-trichloroethane (3:5330). [$\bar{C}$ with 1,1,2-trichloroethane + $AlCl_3$ (1%) at 35–40° for 5 days gives (104) two diastereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., liq. (3:9068) and solid (3:0750).]

With 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). [$\bar{C}$ with acetylene tetrachloride + $AlCl_3$ gives a mixt. from which can be isolated only (104) solid 1,1,2,3,4-pentachlorobutane (3:0750).]

With 1,1,1,2-tetrachloroethane (3:5555). [$\bar{C}$ with *unsym.*-tetrachloroethane + $AlCl_3$ at 40° for 10 days gives (104) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

With pentachloroethane (3:6880). [$\bar{C}$ with pentachloroethane + $AlCl_3$ at 40° for 12 days presumably first forms both 1,1,2,2,3,4,4-heptachlorobutane (3:9056) and 1,1,1,2,3,4,4-heptachlorobutane, but the latter loses HCl and by further reaction and/or resinification is lost in the accompanying resins (104); the HCl thus split out adds (in the pres. of $AlCl_3$) to $\bar{C}$ yielding 1,1,2-trichloroethane which then condenses with more $\bar{C}$ as stated above (104).]

With hexachloropropene (3:6370). [$\bar{C}$ with hexachloropropene + $AlCl_3$ in CH_2Cl_2 soln. yields (105) a single 1,1,2,3,3,4,5,5-octachloropentene-1, b.p. 145–147° at 11 mm., 113–113.5° at 2 mm., $D_{21}^{21} = 1.749$, $n_D^{21} = 1.5607$ (105). This prod. with conc. H_2SO_4 gives (80% yield (105)) a mixt. of pentachlorobutenecarboxylic acids (105).]

Behavior with organic OH or SH derivs. [$\bar{C}$ (1 mole) with C_2H_5SH (2 moles) in alc. KOH (2.6 moles) refluxed ½ hr. gives (yield not stated (106)) 1,2-*bis*-(ethylthio)ethylene, b.p. 170° at 13 mm.]

[$\bar{C}$ (1 mole) with benzyl mercaptan (2 moles) in alc. KOH refluxed 7 hrs. gives (yield not stated (106)) 1,2-*bis*-(benzylthio)ethylene, white ndls. from alc. or AcOH, m.p. 61°; this prod. in CS_2 adds 1 Br_2 giving 1,2-dibromo-1,2-*bis*-(benzylthio)ethane, ndls. from ether, m.p. 73–74°.]

[$\bar{C}$ (1 mole) with thiophenol (2 moles) in alc. NaOEt (2 moles) refluxed 24 hrs., poured into aq., gives (yield not stated (108)) 1,2-*bis*-(phenylthio)ethylene, b.p. 235–242° at 760 mm., pl. from lt. pet., m.p. 62°.]

$\bar{C}$ (1 mole) with *p*-tolylmercaptan (2 moles) in 7% alc. KOH refluxed 3 hrs. gives (90% yield (107)) 1,2-*bis*-(*p*-tolylthio)ethylene, ndls. from alc., m.p. 93°; this prod. in $CHCl_3$ adds 1 mole Br_2 giving (100% yield) 1,2-dibromo-1,2-*bis*-(*p*-tolylthio)ethane, cryst. from pet. ether, m.p. 72° (107).

[For analogous reactn. with $\bar{C}$ of *o*-nitrothiophenol or *p*-nitrothiophenol see (106).]

[$\bar{C}$ (1 mole) with an alk. salt of thiosalicylic acid (*o*-mercaptobenzoic acid) reacts similarly giving (109) (110) cf. (111) (112) 1,2-*bis*-(*o*-carboxyphenylthio)ethylene ("*S,S*-vinylene-

bis-thiosalicylic acid") [Beil. X-128, X_1-(55)]; this prod. with KOH/NaOH at 220–230° gives (113) 3-hydroxythionaphthene (thioindoxyl) [Beil. XVII-110, $XVII_1$-(60)], or by actn. of acid condensing agents (e.g., fuming H_2SO_4, $ClSO_3H$, etc.) yields (114) the important dyestuff thioindigo [Beil. XIX-177, XIX_1-(690).] — Note that the corresp. condens. of $\bar{C}$ with salicylic acid (*o*-hydroxybenzoic acid) or with anthranilic acid (*o*-aminobenzoic acid) *cannot* be effected (112).]

Behavior with other misc. organic reactants. [$\bar{C}$ with paraformaldehyde (1:0080) + conc. H_2SO_4 gives (115) a resin (cf. behavior of 1,1,2-trichloroethylene (3:5170)).]

[$\bar{C}$ (1 mole) with EtMgBr (2 moles) yields (116) C_2H_6 + $BrMgC{\equiv}C{-}MgBr$ + $MgCl_2$.]

[$\bar{C}$ does *not* (117) react with acetyl iodide even after 150 days at 25°.]

COLOR TESTS FOR $\bar{C}$

Ⓟ Color test with α-naphthol/cyclohexanol. $\bar{C}$ (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 2 pellets solid NaOH boiled 25 seconds, cooled, gives after acidification with AcOH or 85% H_2SO_4, stdg. 1 min., and shaking a violet or red-violet color (118). — [Note that under these conditions the response given by methylene (di)chloride (3:5020) is green-blue; by both $CHCl_3$ (3:5050) and CCl_4 (3:5100) is intense blue; by 1,2-dichloroethane (ethylene dichloride) (3:5130) is colorless to pale green; by 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) is intense green-blue; by pentachloroethane (3:5880) is gray-green; by 1,1,2-trichloroethylene (3:5170) is intense green-blue; and by tetrachloroethylene (3:5460) is green (118).]

—— Mercury *bis*-(chloroacetylide) $Hg(-C{\equiv}C-Cl)_2$. Shining white pl. from hot $CHCl_3$; although reported to melt at 185° (119) (120) (121) has also been found (122) to explode *with great violence* well below that temperature, i.e., 174–175° (122). [From $\bar{C}$ with aq. $Hg(CN)_2$ + KOH on shaking at room temp. (91) (123) for 48 hrs. (119), or from $\bar{C}$ in alc. run into a stirred aq. soln. of $HgCl_2$ + NaCN + KOH (120), or from $\bar{C}$ shaken with an aq. soln. of HgO + NaCN + NaOH (122). — Note, however, that in fact this prod. results only from the higher-boilg. (*cis*) stereoisomer of $\bar{C}$ (3:5042) and that the lower-boilg. (*trans*) stereoisomer (3:5028) reacts much more slowly and quite differently to yield mercury *bis*-(α,β-dichloroethylenide), m.p. 50.3° (122). — *Note further that by the above treatment 1,1,2-trichloroethylene* (3:5170) *gives* mercury *bis*-(trichloroethylenide), m.p. 83°, but this prod. is much more sol. in $CHCl_3$ than the analogous material from $\bar{C}$ (for use in detect. of $\bar{C}$ in pres. of 1,1,2-trichloroethylene see (123)).]

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Dec 20, 1938, *Cent.* **1939**, I 3

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2589 (1913).
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3:5035 1,1-DICHLOROETHANE $CH_3.CHCl_2$ $C_2H_4Cl_2$ Beil. I - 83
(Ethylidene (di)chloride; I_1-(23)
unsym.-dichloroethane) I_2-(52)

B.P.			F.P.	
57.30°	at 760 mm.	(1) (2)	**−96.6°** (1)	D_4^{25} = **1.16790** (1)
57.28–57.34°	cor.	(3)	**−96.7°** (2)	D_4^{20} = **1.17570** (1)
57.25°	at 760 mm.	(4)	**−97.4°** (8)	**1.1755** (8)
57.0–57.1°		(5) (6) (7)	**−99°** (9)	D_4^{15} = **1.18350** (1)
57.1°	at 760 mm.	(8)		n_D^{20} = **1.41638** (8)
56.7–56.9°	at 743 mm.	(9)		n_D^{15} = **1.41975** (1)

Liquid. — [For b.p. at various press. from 70–277 mm. see (11).] — Alm. insol. aq. [for precise data see (5) (6) (7) (11).] — [For f.p./compn. data of mixts. with 2,2-dichloropropane (3:7140) see (10).] — [For use as dry cleaning fluid see (12); for use as corrosion inhibitor for alk. on tinned metal see (13).]

C̄ forms with EtOH (1:6130), b.p. 78.3°, a const.-boilg. mixt., b.p. 54.6°, contg. 88.5 wt. % C̄ (4); C̄ forms with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 56.6°, contg. 82 wt. % C̄ (4); C̄ forms with *ter*-butyl alc. (1:6140), b.p. 82.5°, a const.-boilg. mixt., b.p. 57.1°, contg. 94 wt. % C̄ (14); C̄ forms with acetone (1:5400), b.p. 56°, a const.-boilg. mixt., b.p. 57.55°, contg. 70 wt. % C̄ (14); C̄ forms with CS_2, b.p. 46.3°,

Cent.: French 840,867, May 5, 1939; *Cent.* **1939**, II 4349; *C.A.* **34**, 1781 (1940). (75) Mahncke, Noyes, *J. Am. Chem. Soc.* **58**, 932–933 (1936). (76) Biesalski, *Z. angew. Chem.* **37**, 317 (1924). (77) Muller, Schumacher, *Z. Elektrochem.* **43**, 807–808 (193
chim. Belg. **27**, 334–343 (1913); *Cent.* **1914**, I 618. (79) C
289–294 (1912); 28, 234–240 (1914); *Cent.* **1912**, II 1006; 1
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(81) Ghosh, S. K. Bhattacharyya, S. C. Bhattacharyya, *Z. physik. Chem.* **B-32**, 145–157 (1936). (82) Hofmann, Kirmreuther, *Ber.* **42**, 4483 (1909). (83) Herz, Rathmann, *Ber.* **46**, 2589 (1913). (84) Bruner, Fischler, *Z. Elektrochem.* **20**, 84 (1884). (85) Müller, Hönn, *J. prakt. Chem.* (2) **133**, 290 (1932). (86) Prins, *Rec. trav. chim.* **45**, 80–81 (1926). (87) Brooks, Humphrey, *J. Am. Chem. Soc.* **40**, 843–844. (88) Lepouse, *Bull. soc. chim. Belg.* **34**, 133–142 (1925). (89) Ott (to Chem Fabrik vorm. Weiler-ter-Meer, Ger. 362,744, Oct. 31, 1922; *Cent.* **1923**, II 1246; *C.A.* **18**, 1129 (1924). (90) Klimont, *Chem. Ztg.* **46**, 521–522 (1922).

(91) Hofmann, Kirmreuther, *Ber.* **42**, 4233–4234 (1909). (92) Thron, *Chem. Ztg.* **48**, 142 (1924). (93) Fromm, Landmann, *Ber.* **56**, 2292 (1923). (94) Stähler, *Ber.* **47**, 912 (1914). (95) Steinkopf, Hühner, *Ber.* **75**, 1326–1327 (1942). (96) Burrows, Hunter, *J. Chem. Soc.* **1932**, 1358–1359 (97) Alder, Rickert, *Ann* **543**, 10–11, 26–27 (1940). (98) Lehmann (to I.G.), Ger. 715,069, Dec. 16, 1941; Cent. **1942**, I 2584; C.A. **38**, 2051 (1944). (99) Heilbron, Heslop, Irving, *J. Chem. Soc.* **1936**, 782–783. (100) Prins, Engelhard, *Rec. trav. chim.* **54**, 307–312 (1935).

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(121) Hofmann, Kirmreuther, *Ber.* **41**, 316 (1908). (122) FitzGibbon, *J. Chem. Soc.* **1938**, 1218–1222. (123) Schmalfuss, Werner, *Z. anal. Chem.* **97**, 314–317 (1934).

3:5035 1,1-DICHLOROETHANE $CH_3.CHCl_2$ $C_2H_4Cl_2$ Beil. I - 83
(Ethylidene (di)chloride; I_1-(23)
unsym.-dichloroethane) I_2-(52)

B.P.			F.P.			
57.30°	at 760 mm.	(1) (2)	**−96.6°**	(1)	D_4^{25} = **1.16790**	(1)
57.28–57.34°	cor.	(3)	**−96.7°**	(2)	D_4^{20} = **1.17570**	(1)
57.25°	at 760 mm.	(4)	**−97.4°**	(8)	**1.1755**	(8)
57.0–57.1°		(5) (6) (7)	**−99°**	(9)	D_4^{15} = **1.18350**	(1)
57.1°	at 760 mm.	(8)			n_D^{20} = **1.41638**	(8)
56.7–56.9°	at 743 mm.	(9)			n_D^{15} = **1.41975**	(1)

Liquid. — [For b.p. at various press. from 70–277 mm. see (11).] — Alm. insol. aq. [for precise data see (5) (6) (7) (11).] — [For f.p./compn. data of mixts. with 2,2-dichloropropane (3:7140) see (10).] — [For use as dry cleaning fluid see (12); for use as corrosion inhibitor for alk. on tinned metal see (13).]

C̄ forms with EtOH (1:6130), b.p. 78.3°, a const.-boilg. mixt., b.p. 54.6°, contg. 88.5 wt. % C̄ (4); C̄ forms with isopropyl alc. (1:6135), b.p. 82.45°, a const.-boilg. mixt., b.p. 56.6°, contg. 82 wt. % C̄ (4); C̄ forms with *ter*-butyl alc. (1:6140), b.p. 82.5°, a const.-boilg. mixt., b.p. 57.1°, contg. 94 wt. % C̄ (14); C̄ forms with acetone (1:5400), b.p. 56°, a const.-boilg. mixt., b.p. 57.55°, contg. 70 wt. % C̄ (14); C̄ forms with CS_2, b.p. 46.3°,

const.-boilg. mixt., b.p. 44.75°, contg. about 28 wt. % $\bar{C}$ (14). [For study of b.p., *D*, and vapor-liq. equil. of binary mixts. of $\bar{C}$ with $CHCl_3$ (3:5050), CCl_4 (3:5100), or with 1,2-dichloroethane (3:5130) see (27).]

[For soly. of aq. in $\bar{C}$ see (29); for adsorption of $\bar{C}$ by activated carbon at various temps. see (30).]

[For prepn of $\bar{C}$ from acetaldehyde (1:0100) with PCl_5 see (15) (16) (17); from vinyl chloride (3:7010) by catalyzed addn. of HCl see (18) (19) (20) (note that in absence of catalyst addn. of HCl to vinyl chloride is very slow (21)); for formn. of $\bar{C}$ (22.6%) together with other products from ethane with Cl_2 above 290° in pres. of ethylene see (28).]

$\bar{C}$ on passing over pumice at dark red heat yields (22) (23) vinyl chloride (3:7010) + HCl.

[For reactn. of $\bar{C}$ + $AlCl_3$ with 1,2-dichloroethylene (3:5030) or with trichloroethylene (3:5170) yielding polychlorobutanes see (24); for reactn. of $\bar{C}$ with amylidene disodium see (25).]

$\bar{C}$ on htg. in s.t. at 120° with aq. alc. soln. of 2 moles Na (or K) α-naphtholate yields (26) acetaldehyde di-α-naphthylacetal, ndls., m.p. 117° (26).

3:5035 (1) Timmermans, Martin, *J. chim. phys.* **23**, 770–771 (1926). (2) Timmermans, *Bull. soc. chim. Belg.* **25**, 300–327 (1911); *Cent.* **1911**, II 1015. (3) Maryott, Hobbs, Gross, *J. Am. Chem. Soc.* **63**, 660 (1941). (4) Lecat, *Rec. trav. chim.* **46**, 242 (1927) (5) Gross, *Physik. Z.* **32**, 589 (1931). (6) Gross, *Z physik. Chem.* **B-6**, 215–220 (1929). (7) Gross, *J. Am. Chem. Soc.* **51**, 2362–2365 (1929). (8) Henne, Hubbard, *J. Am. Chem. Soc.* **58**, 404 (1936). (9) Schiff, *Ann.* **220**, 96 (1883). (10) van de Vloed, *Bull soc chim. Belg.* **48**, 260 (1939).

(11) Rex, *Z physik. Chem.* **55**, 358 (1906). (12) Parkhurst (to Stand. Oil of Cal.), U.S. 1,948,015, Feb. 20, 1934; *Cent.* **1934**, II 863; *C.A.* **28**, 2034 (1934). (13) Nitti (to E R Squibb [illegible] 4956 (1939). (14) Lecat, [illegible] –324 (1858). (16) Wurtz, [illegible] 12 (1860). (18) Nutting, Petrie, Huscher (to Dow Chem Co), U S. 2,007,144, July 2, 1935, *Cent.* **1935**, II 3829; *C.A.* **29**, 5460 (1935). (19) Wibaut, van Dalfsen (to Dow Chem. Co), U S. 1,990,968, Feb. 12, 1935; *Cent.* **1935**, II 2580, *C.A.* **29**, 2178 (1935). (20) Coleman (to Dow Chem. Co), U.S 1,900,276, March 7, 1933; *Cent.* **1933**, I 3364; *C A* **27**, 2965 (1933).

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3:5042 ***cis*-1,2-DICHLOROETHYLENE** (*cis*-Acetylene dichloride)

$$\begin{array}{c} H—C—Cl \\ \| \\ H—C—Cl \end{array}$$

$C_2H_2Cl_2$ Beil. I — I_1-(78) I_2-(159)

B.P.			F.P.			
60.33–60.38° cor.		(1)	−82°	(22)	D_4^{25} = 1.2743 (12)	
60.25°	at 760 mm.	(2) (3) (4)	−81°	(17)	D_4^{20} = 1.2820 (12)	
60.2°	at 760 mm.	(5)	−80.5°	(3)	D_4^{15} = 1.2913 (2)	
60.14°		(6)			1.2896 (12)	
60.1°		(7)				
60.0–60.5°		(8) (9)				n_D^{25} = 1.44284 (11)
59.9–60.1°	at 760 mm.	(10)				n_D^{17} = 1.44992 (15)
59.9°	at 768 mm.	(11)				n_D^{15} = 1.45189 (3)
59.8°	at 763 mm.	(12)				
59.6°	at 745 mm.	(13)				
59.5–60.1°	at 753 mm.	(14)				
59.4–59.7°	at 749.6 mm.	(15)				
59.4–60.4°		(39)				
59°		(16)				

See also both *trans*-1,2-dichloroethylene (3:5028) and ordinary (mixt. of *cis* and *trans*) 1,2-dichloroethylene (3:5030); the following text is restricted to studies on substantially pure *cis*-stereoisomer.

Note carefully that 1,2-dichloroethylene is *not* the same as ethylene (di)chloride (3:5130) (there are an almost incredible number of errors in the literature involving this point); neither is it the same as the now very important 1,1-dichloroethylene (vinylidene (di)-chloride) (3:5005).

GENERAL DATA ON C̄

Note that substantially pure C̄ is commercial solvent in U.S.A. under designation "Di-60" (referring to the two chlorine atoms and the b.p.) [for study of thermal conductivity and for tabulation of constants of comml. C̄ see (18). — For toxicity of C̄ see (40) (23). — For use of C̄ in extraction of caffeine from coffee see (24)].

[For data on vap. press. of C̄ over temp. range 27–59.8° see (12). — For data on flammability of C̄ see (19). — For ebullioscopic constant of C̄, viz., 34.4° (for 1 mole solute in 100 g. C̄), see (20).]

Binary systems contg. C̄. (See also below under azeotropes.) — [C̄ + *trans-1,2-dichloroethylene* (3:5028): for use of n_D^{25} in detn. of composition of mixt. see (11); for f.p./compn. data (eutectic, f.p −91°, contg. about 71% C̄) see (17). — For f.p./compn. data on binary systems *C̄ + ethylene (di)chloride (3:5130), C̄ + 1,1,2,2-tetrachloroethane* (acetylene tetrachloride) (3:5750), or *C̄ + ethylene (di)bromide* see (17). — For study of soly. of various other *cis/trans* isomers in C̄ see (5).]

Quaternary systems contg. C̄. [For study of system contg. C̄ + $CHCl_3$ (3:5050) + trichloroethylene (3:5170) + EtBr (eutectic, f.p. −139.1°, contg. 13.8 wt. % C̄ + 19 7 wt. % $CHCl_3$ + 21.6 wt. % trichloroethylene + 44.9 wt. % EtBr recommended as a non-inflammable mixt. for low-temp. cryostats) see (22); for mixt. of the above four compds. + methylene dichloride (3:5020) (similarly recommended) see (22).]

Azeotropes contg. C̄. *Binary azeotropes — C̄ with aq* forms a const.-boilg. mixt., b.p 55 3°, contg. 96.65% C̄ (41) (42). — *C̄ with EtOH* (1:6130) forms a const.-boilg. mixt., b.p. 57.7° at 760 mm. (21) (41) (42), contg. 90 20% C̄ (41) (42) = 81.4 mole % C̄ (21)

Ternary azeotropes. C̄ with EtOH (1:6130) + aq. forms a const.-boilg. mixt, b p. 53.8°, contg. 90.50% C̄ + 6.65% EtOH + 2.85% aq. (41) (42).

PREPARATION OF $\bar{C}$

Pure $\bar{C}$ is usually obtd. by careful fractional distillation at ord. press. of the mixt. of *cis* and *trans* stereoisomers comprising ord. 1,2-dichloroethylene (3:5030) [for brief comments on this mode of sepn. see (1) (2) (6) (7) (8) (9) (10) (11) (13) (15) (27); note that some workers (13) recommend distn. in atmosphere of CO_2. — For detn. of the % compn. of mixts. of $\bar{C}$ with its stereoisomer by means of n_D^{25} see (11); by means of dielectric const. see (13) (27)].

[For study of possibility of sepn. of $\bar{C}$ from its stereoisomer by differential adsorption on silica gel see (25).]

[For prepn. of $\bar{C}$ from pure *trans* stereoisomer (3:5028) by isomerization with 6 wt. % Br_2 in dark for 24 hrs. followed by subsequent fractionation of the resultant mixt. see (11).]

ISOMERIZATION OF $\bar{C}$

$\bar{C}$ under the influence of heat, light, or various catalysts in part isomerizes to *trans*-1,2-dichloroethylene (3.5028). — [For study of thermal isomerization of $\bar{C}$ in vapor phase at 185–275° (26), up to 350° (27), up to 975° (28), in liquid phase or in various solutions (13) see indic. refs.; note that the equilibrium mixt. at 300° conts. 60.8 ± 0.7% $\bar{C}$, at 350° conts. 59 4 ± 0.3% $\bar{C}$ (27), at 975° conts. 52.3% $\bar{C}$ (28) — For study of kinetics of thermal isomerization see (29).]

[For patent on isomerization of pure $\bar{C}$ to a mixt. contg. 18% *trans* stereoisomer by means of a small amt. Br_2 at 30° or above in pres. of cat. or in vapor phase at not over 300° see (30).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Reactions with inorganic compds. $\bar{C}$ (in vapor phase at 95° in light of 4360 Å (31)) with Cl_2 (in absence of O_2), or $\bar{C}$ as liquid with SO_2Cl_2 (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (8), adds 1 mole halogen giving (85% yield (8)) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3.5750).

$\bar{C}$ with Br_2 in sunlight adds 1 mole halogen yielding (2) (32) 1,2-dibromo-1,2-dichloroethane [Beil. I-93, I_1-(29), I_2-(64)], b p. 195° at 760 mm. (3) (33), b.p. 79.0–79.5° at 15 mm. (2). — [For extensive study of influence of O_2 and other factors see (32); for study of kinetics in CCl_4 soln. see (2) (34) (35); note that rate of addn. of Br_2 either directly or in CCl_4 is half as great as for the stereoisomeric *trans* form (3:5028) but that it is increased in pres. of $SbBr_3$ (35).]

$\bar{C}$ in the absence of $AlCl_3$ or other cat. does not add dry HCl; satn. of $\bar{C}$ with dry HCl changes n_D^{25} by an amount corresp. to only 2% change in compn. (11).

[$\bar{C}$ with alc. KOH splits out 1 HCl yielding chloroacetylene (3:7000); note that this reactn. is about 20 times as fast for $\bar{C}$ as for its *trans* stereoisomer (2)]

$\bar{C}$ with aq. $NaOH/Hg(CN)_2$ behaves quite differently from its *trans* stereoisomer (3:5028): on shaking at room temp. with specified concns. (16) $\bar{C}$ begins to react within 30 min., losing 1 HCl and pptg mercuric *bis*-(chloroacetylide), $Hg(—C{\equiv}C—Cl)_2$; this prod. cryst. from $CHCl_3$ (36) (37) (38) in white shining pl. with characteristic acetylene-like odor and although alleged to melt at 185° (36) (37) has also been found to explode *with great violence* well below that temp , i.e., 174–175° (16).

Reactions with organic compds. [$\bar{C}$ with C_6H_6 + Al/Hg at 0° gives same prods. as does the ordinary (mixture) 1,2-dichloroethylene (3:5030) (presumably indicating partial isomerization of $\bar{C}$); these prods. include dibenzyl, triphenylethane, tetraphenylethane, etc. (15).]

3:5042 (1) [illegible]

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3:5050 CHLOROFORM (Trichloromethane) $CHCl_3$ Beil. I - 61, I_1-(9), I_2-(14)

B.P.			F.P.			
[62.0°	at 760 mm.	(2)]	−63.0°	(27) (28) (61)	$D_4^{30} = 1.47060$ (12)	$n_D^{25.4} = 1.44295$ (49)
[61.97°	at 760 mm.	(3)]	−63.2°	(29) (26)	$D_4^{25} = 1.47988$ (12)	
					1.47972 (20)	
[61.64°	at 760 mm.	(4) (1)]	−63.3°	(30)	1.47955 (45)	
			−63.41°	(31)	1.4794 (43)	
[61.40°	at 758 mm.	(5)]	−63.495°	(32)	1.4793 (44)	
61.36–61.38°	at 763.9 mm.	(6)	−63.5°	(33) (34) (35) (36) (37) (12) (38)	1.4791 (21)	
					1.4789 (19)	
					1.4702 (46)	
61.33–61.38°	at 760 mm.	(7)	−63.57°	(17)		$n_D^{25} = 1.44460$ (50)
61.3° u.c.	at 759 mm.	(8)	−63.6°	(39)		1.4433 (51)
61.28°	at 761 mm.	(9)	−63.7°	(40)		1.4431 (19)
61.20–61.25°	at 760 mm.	(10)	−64.19°	(41)		1.44309 (52)
61.21°	at 760 mm.	(11)	−66.5°	(42)		1.4424 (44)
61.20°	at 760 mm.	(12) (1) (15) (16)	See Note 2.			$n_D^{24.8} = 1.4437$ (43)
						$n_D^{22.4} = 1.44500$ (53)

B.P. (*contd.*)

61.152°	at 760 mm.	(13)
61.15°	at 760 mm.	(14)
61.09°	at 760 mm.	(17)
61.07–61.09°	at 760 mm.	(18)
61.05–61.10°	at 760 mm.	(50)
61.05–61.10°	at 758 mm.	(19)
61.0°		(20)
61.0°	at 755 mm.	(21)
60.94–60.96°	at 755 mm.	(22)
60.93°	at 744.2 mm.	(4)
60.9°	at 754.3 mm.	(23)
60.9°	at 732 mm.	(24)
60.7°	at 743.8 mm.	(25)
60.39°	at 735.6 mm.	(4)
56.0°	at 664 mm.	(21)
55.10°	at 632.8 mm.	(26)
53.8°	at 616 mm.	(21)
50.5°	at 550 mm.	(21)
47.0°	at 481 mm.	(21)
42.8°	at 416 mm.	(21)
40.40°	at 371.8 mm.	(26)
38.0°	at 342 mm.	(21)
33.0°	at 287 mm.	(21)
28.115°	at 221.8 mm.	(26)
27.0°	at 223 mm.	(21)

See Note 1.

D_4^{20} = 1.48921 (13)
1.48917 (12)
1.48913 (13)
1.48901 (13)
1.4890 (47)
1.4889 (10)
(48)
1.4817 (62)

n_D^{20} = 1.44637 (10)
1.4458 (7)
1.446 (17)

$D_4^{18.85}$ = 1.4828 (54)

$n_D^{18.85}$ = 1.44572 (54)

D_4^{15} = 1.49845 (12)
1.4963 (21)

n_D^{15} = 1.44858 (12)
1.4466 (55)

$n_D^{12.5}$ = 1.4506 (56)

See Note 3.

Note 1. For b.p. of C̃ at various pressures from 355–2347 mm. see (13); for vap. press. of C̃ over range −62.1° to 0° (57) or −64.2° to −10.7° (58) see indic. refs.

Note 2. For influence of high press. on m.p. of C̃ see (33); for study of rate of solidification see (35).

Note 3. For D_t^t over range −61.3° to +59.8° see (59).

[For extraordinarily comprehensive reviews of the history and general chemistry of C̃ see (1) (60).]

[*See also methylene (di)chloride* (3:5020) *and carbon tetrachloride* (3:5100).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C̃

Various Solubility Relations

With water. C̃ is only very slightly sol. aq. and is eas. volat. with steam; e.g., 100 g. aq. at 15° dissolves 0.852 g. C̃ (18); water satd. with C̃ conts. at 20° 0.8% C̃ (63) cf. (64). For studies of soly. of aq. in C̃ at 0° (65), 20° (63), 25° (65), and 30° (65) see indic. refs.; note that at 20° C̃ satd. with aq. conts. 99.8% C̃ and has D_4^{20} = 1.486 (63).

With various inorganic compounds. [For data on soly. in C̃ of H_2 (66), O_2 (78), HCl (67) (68) (69) (79), HBr (68) (69), H_2S (67), NH_3 (67), CO_2 (70) (80) (81), N_2O (81), and NO_2 (70) see indic. refs. — For data on soly. of I_2 in C̃ see (71) (72) (73) (74); for study of nature of I_2 solns. in C̃ see (75); for soly. of I_2 in vapor of C̃ see (76).]

With organic materials. [For study of absorption of vapor of C̃ by kerosene see (77).]

BINARY SYSTEMS CONTAINING $\bar{C}$

(See also azeotropes containing $\bar{C}$)

$\bar{C}$ with various inorganic compounds. $\bar{C}$ + *aq.*: for soly. data and diag. see (64); note that a previously described (82) hydrate of $\bar{C}$ could *not* be confirmed (64). — $\bar{C}$ + Cl_2: for f.p./compn. data and diag. (note that 4 different compounds are formed) see (34). — $\bar{C}$ + Br_2: for f.p./compn. data and diag. see (34) (36) (note that no compds. are formed and that eutectic has m.p. −72° (34) with about 86 mole % $\bar{C}$).

$\bar{C}$ with org. cpds. of Order 1. $\bar{C}$ + *n-hexane* (1:8530): for f.p./compn. data see (83); for densities over range −90° to +60° see (85). — $\bar{C}$ + C_6H_6 (1:7400): for f.p./compn. data and diag. see (38); for D_4^{25}/compn. and n_D^{25}/compn. data over entire range see (19); for D_{25}^{25}/compn. data see (18); for liq. vapor equil. see (19) (117) (112) (124). — $\bar{C}$ + *toluene* (1:7405): for f.p./compn. data see (83); for data on specific gravity of system from 15-25° see (86); for study of liq.-vapor equil. see (123). — $\bar{C}$ + *cyclohexane* (1:8405): for f.p./compn. data see (83); for D_4^{20} compn. see (47).

$\bar{C}$ + *MeOH* (1:6120): for f.p./compn. data see (37) (84); for D_-^{25}/compn. and n_D^{25}/compn. see (44). — $\bar{C}$ + *EtOH* (1:6130): for D_4^{25}/compn. data see (45) (46). — $\bar{C}$ + *benzyl alc.* (1:6480): for density/compn. data over entire range see (87).

$\bar{C}$ + *diethyl ether* (1:6110): for f.p./compn. data and diag. see (42) (88); for D_4^{20}/compn. see (47). — $\bar{C}$ + *diisopropyl ether* (1:6125): for D_4^{20}/compn. see (47). — $\bar{C}$ + *dioxane-1,4* (1:6400): for D_4^{20}/compn. see (47). — $\bar{C}$ + *ethylene glycol dimethyl ether* (1:6141): for study of heat of mixing see (89). — $\bar{C}$ + *tetraethylene glycol dimethyl ether:* for study of heat of mixing see (89).

$\bar{C}$ + *dimethyl carbonate* (1:3046): for D_4^{25}/compn. data see (20). — $\bar{C}$ + *diethyl carbonate* (1:3150): for D_4^{25}/compn. data see (20).

$\bar{C}$ + *acetone* (1:5400): for f.p./compn. data see (27); for D_4^{20}/compn. (47), D_4^{25}/compn. (19) (46), n_D^{25}/compn. (19), and $n_D^{25.4}$/compn. (49) data see indic. refs.; for refractive index/compn. for light of various wave lengths see (52).

With org. cpds. of Order 2. $\bar{C}$ + *nitrobenzene:* for f.p./compn. data and diag. (eutectic, f.p. −71.0° conts. 81.5 wt. % $\bar{C}$) see (61). — $\bar{C}$ + *aniline:* for f.p./compn. data and diag. see (27). — $\bar{C}$ + *N,N*-dimethylaniline: for D_4^{25}, D_4^{40}, $n_D^{24.8}$, and $n_D^{39.5}$ over entire range of composition see (43). — $\bar{C}$ + *quinoline:* for D_4^{20}/compn. data see (47).

With org. cpds. of Order 3. $\bar{C}$ + CH_2Cl_2 (3:5020): for f.p./compn. data and diag (eutectic, f.p. −108.4° conts. 29.5 wt. % $\bar{C}$) see (39); for data on b.p., D_4^{20}, and liq.-vapor equil. see (90). — $\bar{C}$ + CCl_4 (3:5050): for f.p./compn. data and diag. (eutectic, f.p. −81.4° conts. 50.6 wt. % $\bar{C}$ (39)) (36) (83) (91) see indic. refs.; for D_4^{20}/compn. (48) (90), D_{25}^{25}/compn. (8), b.p. and liq.-vapor equil. (90) see indic. refs. — $\bar{C}$ + *1,1-dichloroethane* (3:5035): for b.p., D_4^{20}, and liq.-vapor equil. see (90). — $\bar{C}$ + *1,2-dichloroethane* (3:5130): for data on vap. press. (92) and liq.-vap. equil. (93) see indic. refs. — $\bar{C}$ + *1,1,1-trichloroethane* (3:5058): for f.p./compn. data see (94). — $\bar{C}$ + *1,1,2-trichloroethylene* (3:5170): for f.p./compn. data and diag. (eutectic, f.p. −100.2°, conts. 31.2 wt. % $\bar{C}$) see (39). — $\bar{C}$ + *β,β'-dichlorodiethyl ether* (3:6025): for D_4^{20}/compn. data see (47).

With org. cpds. of higher orders. $\bar{C}$ + *1,2-dibromoethane:* for D_4^{20}/compn. data see (47). — $\bar{C}$ + CBr_4: for f.p./compn. data and diag. see (91). — $\bar{C}$ + CHI_3: for vap. press. data see (95). — $\bar{C}$ + CS_2: for f.p./compn. data see (83); for D_{15}^{15} compn. (96) or D_{25}^{25}/compn. (8) see indic. refs.; for liq.-vapor equil. data see (97).

Ternary Systems Containing $\bar{C}$

(See also azeotropes containing $\bar{C}$)

$\bar{C}$ + *acetone* (1:5400) + *H_2O:* for studies of liq. equil. at 25° see (98) (99) (100) (101) (102). — $\bar{C}$ + *acetone* (1:5400) + *MeOH* (1:6120): for ternary b.p. diag. see (103). — $\bar{C}$ + *acetone* (1:5400) + *diethyl ether* (1:6110): for data on refraction see (104). — $\bar{C}$ + *acetone* (1:5400) + *diisopropyl ether* (1:6125). for ternary b.p. diag. see (103).

$\bar{C}$ + *acetone* (1:5400) + *C_6H_6* (1:7400): for ternary b.p. diag. see (103) (19) (105); for refractive data see (104).

$\bar{C}$ + *acetone* (1:5400) + *CH_2Cl_2* (3:5020): for ternary b.p. diag. see (103).

$\bar{C}$ + *acetic acid* (1·1010) + *aq.:* for studies of liq. equil. at 25° see (104) (106) cf. (99). — $\bar{C}$ + *acetic acid* + *lubricating oil:* for studies of liq. equil. at 25° see (107).

$\bar{C}$ + *CH_2Cl_2* (3:5020) + *CCl_4* (3:5100): eutectic, f.p. −111.4°, conts. 27 wt. % $\bar{C}$ + 60 wt. % CH_2Cl_2 + 13 wt. % CCl_4 (39).

Quaternary Systems Containing $\bar{C}$

$\bar{C}$ + *acetone* (1·5400) + *AcOH* (1:1010) + *aq.:* for study of liq. equil. at 25° see (100); for study of use of system in mixed solv. extraction of lubricating oils see (107) (108). — $\bar{C}$ + *trans-1,2-dichloroethylene* (3.5028) + *1,1,2-trichloroethylene* (3:5170) + *C_2H_5Br:* eutectic, f.p −139.1°, conts. 17 7 wt % $\bar{C}$ + 13.8 wt. % *trans*-1,2-dichloroethylene + 21.6 wt. % trichloroethylene + 44.9 wt. % C_2H_5Br (39).

Binary Azeotropes Containing $\bar{C}$

$\bar{C}$ + *H_2O:* $\bar{C}$ forms with aq. a const.-boilg. mixt., b.p. 56.1°, contg. 97.5 wt. % $\bar{C}$ (14).

$\bar{C}$ + *MeOH* (1:6120): $\bar{C}$ forms with MeOH a const.-boilg. mixt , b p. 53.5° (103) (109), contg 87.5 wt. % (103) = 65 mole % (109) $\bar{C}$, cf also (110) (111) (4) (112) (113) — $\bar{C}$ + *EtOH* (1.6130): $\bar{C}$ forms with EtOH a const.-boilg. mixt., b.p. 59.3° at 760 mm. (111), 59.35° at 760 mm. (14), contg. 93.2 wt. % $\bar{C}$ (111) cf. (14) = 84 mole % $\bar{C}$ (111) (see also (4) (110)) of D_{15}^{15}= 1.4112 (14);
study of liq -vap equil. see (45).
alc. a const.-boilg. mixt., b.p. 60
mole % $\bar{C}$ (111). — $\bar{C}$ + *formic acid* (1:1005): $\bar{C}$ forms with formic acid a const.-boilg. mixt , b.p. 59.15° at 760 mm. (115), contg 85 wt. % $\bar{C}$ (115). — $\bar{C}$ + *ethyl formate* (1:3000): $\bar{C}$ forms with ethyl formate a const.-boilg. mixt., b.p 62 8° (116), 62.7° (111) at 760 mm., contg. 87 wt. % $\bar{C}$ — $\bar{C}$ + *methyl acetate* (1:3005): $\bar{C}$ forms with methyl acetate a const.-boilg. mixt., b p. 64.8° at 760 mm (111), contg. 77 wt. % $\bar{C}$ (111); b.p. 63.0° at 726.3 mm. contg. 50 wt. % $\bar{C}$ (117); b.p. 62.6° at 717.5 mm. contg. 56 wt. % $\bar{C}$ (117); for study of constant evapn. system see (125). — $\bar{C}$ + *diisopropyl ether* (1:6125): $\bar{C}$ *forms with di-*
36.5% wt % $\bar{C}$ (103). — $\bar{C}$ + *acetone*
b.p. 64.5° at 760 mm. (109) (103)
wt. % $\bar{C}$ (19) (105), 65 5 mole % $\bar{C}$
(109); b.p. 62.4° at 732.0 mm. contg. 80 wt. % $\bar{C}$ (117); b p. 62 25° at 719 mm. contg 86 wt. % $\bar{C}$ (117) cf also (112); b.p. 61.95° at 716.5 mm contg 85 wt. % $\bar{C}$ (117): for studies of liq.-vapor equil. of $\bar{C}$ + acetone see (19) (105) (117) (112), for study of vap. press. see (26) (49) (118) (119) (120) (121): for study of distn. of $\bar{C}$ + acetone in wetted wall column see (122).

Ternary Azeotropes Containing $\bar{C}$

$\bar{C}$ + *EtOH* (1.6130) + *aq* : $\bar{C}$ forms with EtOH + aq. a ternary const.-boilg. mixt., b p 55.4–55.5° at 760 mm., contg. about 92.5 wt. % $\bar{C}$ + 4 0 wt. % EtOH + 3.5 wt. % aq (14).

indic. refs. For formn. of $\bar{C}$ from various chlorinated ketones by action of alkali hypochlorites (haloform reaction) see (235) (236).]

From alcohols. [For concise reviews of prepn. of $\bar{C}$ from EtOH (1:6130) by action of alkaline hypochlorite solns. see (1) (214); for formn. of $\bar{C}$ from various other primary and secondary alcohols in similar fashion see (237).]

From miscellaneous sources. [*For prepn. of $\bar{C}$ from trichloroacetic acid (3:1150)* by loss of CO_2 under a wide variety of conditions see text of that compound under decarboxylation; from dichloroacetyl chloride (3:5290) on warming with $AlCl_3$ see text of that compound; from mixtures of salts of fatty acids with inorganic chlorides by electrolysis see (238); from lignin with alkali hypochlorite see (239).]

[For prepn. of trichlorodeuteriomethane (deuteriochloroform) ($CDCl_3$) from chloral deuterate + NaOD (443) or from chloral (3:5210) + D_2O + CaO (444) see indic. refs.; for rate of isotopic exchange between $\bar{C}$ and D_2O see (445).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$. [$\bar{C}$ passed at red heat over asbestos (240), over Pt wire at 1000° (241), with 1% I_2 over pumice at red heat (242) cf. (243), or in electric arc (249) undergoes decomposition, and various proportions of carbon, HCl, hexachloroethane (3:4835), hexachlorobenzene (3:4939), tetrachloroethylene (3:5460), pentachloroethane (3:5880), and other products are claimed to result. $\bar{C}$ over htd. TiO_2 gives (245) HCl + CO + hexachlorobenzene (3:4939) + $TiCl_4$. For other studies of pyrolysis of $\bar{C}$ at 368–400° (246), at 425° (247), and at 512° (248) see indic. refs.]

Oxidation of $\bar{C}$. $\bar{C}$ is readily oxidized to carbonyl chloride (phosgene) (3:5000) by air, oxygen, ozone, or chemical oxidizing agents. In view of the extremely toxic character of phosgene, and of the extensive use of $\bar{C}$ in anesthesia, this aspect is of great importance and has been very extensively studied.

By air or oxygen. [For an extensive account of the earlier literature on the oxidation of $\bar{C}$ in air and light see (250). Note that such oxidation is *not* effected by air in absence of light, nor by light in absence of air (251). $\bar{C}$ with limited air in sunlight reacts according to the following equation: $CHCl_3 + O \rightarrow COCl_2$ (3:5000) + HCl (252) but with excess air in sunlight in sense $2CHCl_3 + 5O \rightarrow 2CO_2 + 3Cl_2 + H_2O$ (252). Note that $\bar{C}$ + air over dry KOH gives (253) some phosgene (3:5000). For later studies on the photochemical oxidation of $\bar{C}$ (254) in tropical sunlight (255), including search for possible intermediate peroxides (256) (257), see indic. refs. For studies on chlorine-sensitized photochem. oxidn. of $\bar{C}$ see (258) (259) (260). For oxidn. of $\bar{C}$ by atomic oxygen see (261). The photochem. oxidn. of $\bar{C}$ is repressed by various inhibitors of which EtOH has been most extensively studied (262).]

By ozone. [$\bar{C}$ dissolves ozone yielding a blue soln in which some $\bar{C}$ is gradually oxidized (270) (271) to phosgene; for study of $\bar{C}$ as ozonization solvent see (24).]

By other chemical means. [$\bar{C}$ with $ClSO_3H$ at 120° (263), with $K_2Cr_2O_7 + H_2SO_4$ (264), or with air over CuO at 350–550° (265) gives phosgene (3:5000). Note, however, that $\bar{C}$ with conc. H_2SO_4 above 200° gives (266) (267) $CO + CO_2 + HCl + SO_2$ while $\bar{C}$ with an equimolal mixt. of $H_2S_2O_7 + SO_3$ at 55–60° as directed (268) cf. (269) reacts in sense $CHCl_3 + H_2S_2O_7 + SO_3 \rightarrow CO + 3ClSO_3H$ with $S_2O_5Cl_2$ (pyrosulfuryl chloride) being formed using more SO_3, and H_2SO_4 using less SO_3.]

Inflammability of $\bar{C}$. [For studies of inflammability of $\bar{C}$ in air, oxygen, or O_2/N_2O mixts. see (272) cf. (273).]

Reduction of $\bar{C}$. [$\bar{C}$ with Zn + alc. HCl (274), Zn + AcOH (275), Zn dust + alc. NH_3 (276) (277) (278), Al/Hg + aq. (275), Fe + AcOH (275), or $Si_3H_8 + AlCl_3$ in abs. of air

(279) gives CH_2Cl_2 (3:5020) or further reduction products, e.g., CH_3Cl (3:7005) or CH_4 (280); C̄ with conc. HI on htg. gives (281) CH_2I_2 [Beil. I-71, I_1-(18), I_2-(37)]; C̄ with atomic hydrogen gives (282) CH_3Cl (3:7005) + HCl.]

Substitution of C̄. Note that the text of this section refers only to replacement of the single hydrogen atom of $CHCl_3$.

Fluorination. [The product of replacement of the H atom of C̄ by F (289), viz., trichlorofluoromethane, CCl_3F [*Beil I-64*], *is usually prepd. by indirect means from sources other* than C̄, e g, from CCl_4 (3:5100) + F_2 in pres of As + Br_2 (283). However, beyond noting a few leading articles on its physical consts, including b p. = 23.66° (284), 23 77° (285) at 760 mm., m.p. = −110 48° (284), vapor press (284) (285), liquid density (286), and $P/V/T$ relationships (287), no complete review of CCl_3F and its relatives (cf. (288)) can be given here.]

Chlorination. C̄ on suitable chlorination yields CCl_4 (3:5100). [E.g., C̄ with Cl_2 in sunlight (290) or u.v. light (291) (292) (293) (294), at 260–320° (295), or in pres. of $FeCl_3$ (296) or of aq (297), or C̄ with ICl at 165° (298), or C̄ with aq NaOCl (reaction very slow and incomplete (299)) gives CCl_4 (3:5100). Note, however, that C̄ is *not* chlorinated with SO_2Cl_2 even in presence of organic peroxides (200).]

Bromination C̄ on suitable bromination gives bromotrichloromethane. [E g., C̄ with Br_2 in s t. (301) (298) at 225–275° for 14 hrs. as directed (302), or C̄ with Br_2 in light of 5460 Å (303) or 2650 Å in pres. of O_2 (304), or over carbon at 180–350° (305), or C̄ with aq. NaOBr (299), gives CCl_3Br [Beil I-67, I_2-(31)], b.p. 105° (302), 104.2–104.35° at 758.5 mm. (308), m.p. −21° (302) For prepn. of CCl_3Br from trichloroacetyl bromide by pyrolysis at 400° at ord. press. see (306); for studies of behavior of CCl_3Br with Cl_2 in light (307) (308) or of its halogen-sensitized photochem. oxidn. (309) see indic. refs.]

Iodination. [C̄ with aq. NaOI (299) gives iodotrichloromethane, CCl_3I [Beil. I-71], b p. 142° (299) (310); for prepn of this prod from CCl_4 (3:5100) with AlI_3 in CS_2 (310) or from trichloroacetyl iodide by distn. at ord press. (306) see indic. refs.]

Nitration. [C̄ with HNO_3 in s.t. at 90–100° for 120 hrs. (311) or in boilg. acetyl nitrate (312) gives nitrotrichloromethane (chloropicrin) [Beil. I-76, I_1-(20), I_2-(41)], b.p. 111–112°, but this product is usually prepd. by other means, e.g., from calcium picrate with $Ca(OCl)_2$ (313) (314).]

Nitrosation [No record can be found of any reaction between chloroform and nitrous acid. However, nitrosotrichloromethane [Beil. I_2-(39)] has been obtd. indirectly from sodium trichloromethane sulfinate, CCl_3SOONa, by the action of HNO_3 (315) (316). It is a dark blue liq, b.p. 5 0–5.5° at 70 mm (315), but decomposing on distn at ord. press. The compound is of considerable interest because on reduction with H_2S (315), Al/Hg (315), $SnCl_2$ (316), or SO_2 (316) it yields dichloroformaldoxime, $Cl_2C{=}NOH$, a chemical warfare agent with especially terrifying characteristics.]

Hydrolysis of C̄. C̄ on hydrolysis gives formic acid (1:1005) in such a form that the reaction mixt. is able to reduce Fehling soln. or $NH_4OH/AgNO_3$ even at room temp. or more rapidly on warming (dif. from CCl_4 (3:5100), 1,2-dichloroethane (3:5130), 1,1,2,2-tetrachloroethane (3:5750) and hexachloroethane (3:4835)). Note that, although some CO has been detected, yet formaldehyde (1:0145) is *not* produced (317).

[C̄ with aq. on protracted htg in s t. at 225° gives (318) HCOOH (1:1005) + CO +

[C̄ is also hydrolyzed in alc. alk. solns. even more readily than CCl_4 (3:5100) (321) (101); for use of this principle in estimation of C̄ see above under determination of C̄. For study of kinetics of hydrolysis of C̄ with alc. KOH (325), with $N/10$ KOH in 95% alc. at 90°

(326) cf. (327), or with $Ba(OH)_2$ or TlOH in 50% alc. (328) (327) see indic. refs. Note that C̄ with alc. KOH is also claimed by one worker (253) to give ethylene.]

[For further details on ability of C̄ to reduce Fehling soln. see (317) (329) (330).]

Behavior of C̄ with inorganic salts. [C̄ with $AlCl_3$ gives a gummy hygroscopic addn prod. which with aq. regenerates C̄ (331), but C̄ with $AlBr_3$ is more or less (yields: 58-90% (332), 100% (333)) converted to bromoform [Beil. I-68, I_1-(16), I_2-(33)], b.p. 149.55° at 760 mm. (334), m.p. 8.05° (334), D_4^{25} = 2.87757 (334), D_4^{20} = 2.89054 (334), D_4^{15} = 2.90350 (334), n_D^{15} = 1.60088 (334).]

[C̄ with CaI_2 in s.t. at 100° is partially converted (335) to CHI_3, but C̄ with aq. KI even in pres. of Cu decomposes yielding (336) $CH_4 + H_2 + CO + CO_2$.]

[For leading reference on behavior of C̄ with various metal fluorides see (337).]

Behavior of C̄ with metals. [C̄ with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. For studies of the explosion of C̄ with alkali metals see (338) (339) (340); for further data on explosions of C̄ with Li, Na, K, Ca, Sr, Ba, and Mg, especially with reference to sensitivity to mechanical shock, see (341). C̄ with molten Na at 260–370° as directed (342) gives C̄ + H_2 + CH_4 with smaller amts. of C_2H_6, C_2H_4, and C_2H_2; for study of C̄ with Na vapor see (343).]

[For study of hazards of behavior of $CHCl_3/CCl_4$ mixts. with Al or Mg see (344); for extensive study of corrosion of metals by C̄ see (345).]

[Note that C̄ with Mg in boilg. ether does *not* react, even in pres. of various catalysts (346).]

Behavior of C̄ with various organic reactants. *With carbon monoxide.* [C̄ with CO + water vapor above 200° in pres. of suitable cat. as directed is claimed (347) to give acetic acid (1:1010); C̄ with CO + $AlCl_3$ at 150° and 900 atm. for 6 hrs. gives (21% yield (348)) dichloroacetyl chloride (3:5290).]

With hydrocarbons. [C̄ (excess) with octene-1 (1:8375) in pres. of small amts. (0.02 mole) of dibenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (349) 1,1,1-trichlorononane; under similar conditions C̄ adds to one of the unsatd. linkages of diallyl (1:8045) giving 8,8,8-trichloroheptene-1. — (For other addns. of C̄ to unsatd linkages see below).]

[C̄ with C_6H_6 (excess) in pres. of $AlCl_3$ (350) (351) (352) (353), $FeCl_3$ (354), chromium powder (355), or Al powder (356) gives triphenylmethane (1:7220); other aromatic hydrocarbons presumably give analogous results but cannot be detailed here.]

With saturated halohydrocarbons. [C̄ (1.2 moles) with EtBr (3.8 moles) + $AlCl_3$ (0.07 mole) on htg. as directed (357) gives EtCl (3:7015) + 90% yield $CHBr_3$ (for physical constants see above under behavior of C̄ with inorganic salts ($AlBr_3$)). — C̄ (1 mole) with MeI (3 moles) + $AlCl_3$ (0.04 mole) on similar treatment gives MeCl (3:7005) + (95% yield (357)) iodoform, m.p. 119°. — C̄ with $CHBr_3$ + 5–10% KCl in pres. of moistened $AlCl_3$ under CO_2 in s.t. at 135° for 14 hrs. undergoes a redistribution reaction giving (358) 17% C̄ + 43% $CHCl_2Br$ + 31% $CHClBr_2$ + 9% $CHBr_3$.]

With unsaturated halohydrocarbons. [C̄ (3 wt. pts.) with ord. 1,2-dichloroethylene (3:5030) + $AlCl_3$ (0.25 wt. pt.) stirred with sand for 20 hrs at 30° (359) cf. (360) (361) (362) gives (yields: 63% (359), 70–75% at 50° (360), 46% at 17° in 22 hrs. (360)) 1,1,2,3,3-pentachloropropane (3:6280).]

[C̄ with 1,1,2-trichloroethylene (3:5170) + $AlCl_3$ at 20° gives (361) (362) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g., 50–60°, yield is greatly diminished and several other prods. (361) are formed.]

[C̄ (2 moles) with 1,1,2,2-tetrachloroethylene (3:5460) + $AlCl_3$ (0.2 mole) refluxed 15–20 hrs. gives (85–93% yield (363)) (364) (365) (366) (367) (368) (369) 1,1,1,2,2,3,3-

heptachloropropane (3:0200); for study of equil. of system $\tilde{C}$ + tetrachloroethylene (3:5460) + *unsym.*-heptachloropropane (3:0200) see (370).]

With unsaturated nitriles. [$\tilde{C}$ with acrylonitrile (vinyl cyanide) in pres. of trimethylbenzyl-ammonium hydroxide at 0–5° for 24 hrs or solid KOH at 0–5° for 4 hrs. adds to unsatd. linkage giving (11–12% yield (371)) (372) γ,γ,γ-trichloro-*n*-butyronitrile, m.p 41°, b p 214–216° at 760 mm , 90–95° at 12 mm (371) (372).]

With alcohols or alcoholates. [$\tilde{C}$ with MeOH over cat. at 200–350° gives (373) MeCl (3:7005), $\tilde{C}$ with EtOH under similar conditions gives (373) EtCl (3:7015).]

[$\tilde{C}$ with Na alcoholates gives the corresp trialkyl orthoformates. E.g., $\tilde{C}$ with $NaOCH_3$ gives (374) (375) trimethyl orthoformate (1:3087); $\tilde{C}$ with $NaOC_2H_5$ gives (27–31% yield (376), 36% (377)) (374) (375) triethyl orthoformate (1 .3241); orthoformate esters of higher alcs are similarly prepd cf (374) (377) For study of behavior of $\tilde{C}$ with mixts. of sodium alcoholates see (378); *for treatise on chemistry of aliphatic orthoesters see* (379).]

With mercaptans or mercaptides [$\tilde{C}$ with $NaSCH_3$ should yield trimethyl trithioorthoformate [Beil II_1-(39)], m.p. 16° (380), b p 220° dec (380), 103–104° at 12 mm (381), 96° at 9 mm. (380), n_D^{15} = 1.5696 (381), but this prod has been reported only by other means, e g , from CCl_4 (3:5100) with $NaSCH_3$ (381) and from anhydrous HCOOH (1:1005) with CH_3SH in s t at ord. temp. (380)]

[$\tilde{C}$ with $NaSC_2H_5$ gives (382) (383) (386) triethyl trithioorthoformate [Beil. II-93, II_1-(39)], b p 235° dec (380), 174° at 760 mm (384), 136.5° at 23 mm. (385), 133° at 21 mm. (386), 126.5–128° at 12 mm. (381), 127–128° cor. at 12 mm (387), D_4^{20} = 1.053 (386), n_D^{15} = 1 5410 (381), but this product is usually prepd by indirect means, e.g., from anhydrous HCOOH (1:1005) with C_2H_5SH in pres. of dry HCl (384) (385) or from CCl_4 (3:5100) with $NaSC_2H_5$ (381).]

With phenols or phenolates $\tilde{C}$ with phenols (or with substituted phenols having at least one free ortho or para position) in presence of aq alk. condenses with eventual introduction *of the formyl radical and formn. of phenolic aldehydes (Reimer-Tiemann reaction* (388)). The countless recorded examples of this reaction cannot be detailed here but the following leading references will be found useful. [For modern studies of the Reimer-Tiemann reaction see (389) (390); for studies of influence of substituents in the phenolic component see (391) (392) (393) (394) (395); for extension of the Reimer-Tiemann reaction to other classes such as substituted indoles (396), thiazoles (397) see indic. refs.; for application to β-naphthol (1:1540) giving (38–48% yield (398)) 2-hydroxy-1-naphthaldehyde, m.p. 79–80°, *to β-tetralol (5,6,7,8-tetrahydronaphthol-2)* (399) *see indic refs ; for* studies on theory of Reimer-Tiemann reaction see (400) (401) (402).]

[$\tilde{C}$ with dry KOC_6H_5 at 110° for 4 hrs. under N_2 gives (15% yield (403)) triphenyl orthoformate [Beil VI-152, VI_1-(153)], ndls. from alc., m p. 76–77° (404), 75° (403), 71.5° (405); note that this prod is also formed (405) in the Reimer-Tiemann reaction cf. (390)]

With aldehydes or ketones. $\tilde{C}$ with aromatic (but not aliphatic (406)) alde[illegible]
of aq KOH undergoes addition yielding trichloromethyl-ar[illegible]
benzaldehyde (1 .0195) + aq KOH gives (16% [illegible]
phenyl-carbinol [Beil. VI-476, VI_1-(237), [illegible] at 15 mm.
(400) cf. (406) (corresp acetate, m p. 87 [illegible] [illegible]oate, m p 97.5° (409); corresp. *p*-nitrobenzoate, m p. 100° (410)) [illegible] [an]alogous behavior of $\tilde{C}$ + alkali with *o*-chlorobenzaldehyde (3:6410) (411), *m*-chlorobenzaldehyde (3:6475) (412), *p*-chlorobenzaldehyde (3:0765) (413), *p*-tolualdehyde (1:0215) (412), and furfural (1:0185) (406) see indic. refs. Note that trichloromethyl-aryl-carbinols are also obtd by reaction of arom. hydrocarbons with chloral (3:5210) q v.]

[$\tilde{C}$ with acetone (1:5400) in pres. of dry powdered KOH (0 5 mole) below 0° (414) or 2–3° (415), or KOH in alc. as directed (416), or even $NaNH_2$ (418) gives (yields: 25% (416),

23% (414)) (417) (415) 1,1,1-trichloro-2-methylpropanol-2 (β,β,β-trichloro-*ter*-butyl alcohol = "Chloretone") (3:2662) q.v.; note that use of NaOH lowers the yield (414) and that $Ca(OH)_2$ (416), $Zn(OH)_2$ (414), or $Al(OH)_3$ (414) yields no such product; note also that the crude prod. contains some diacetone alcohol (1:6423) best removed by treatment with aq. (416) since otherwise it forms with the "Chloretone" a const.-boilg. mixt.]

[C̄ (2 moles) with ethyl methyl ketone (1:5405) in pres. of dry powdered KOH (419) or of $NaNH_2$ (418) gives (13.5% yield (419)) by addition 1,1,1-trichloro-2-methylbutanol-2 [Beil. I_2-(424)], b.p. 162–165° (418), 110–113° dec. at 620 mm. (419), D_4^{20} = 1.2128 (419), n_D^{20} = 1.4460 (419). Note, however, that analogous addition of C̄ does *not* occur with diethyl ketone (1:5420) (420), di-*n*-propyl ketone (1:5447) (420), ethyl *n*-propyl ketone (420), methyl isobutyl ketone (1:5430) (420), or methyl phenyl ketone (acetophenone) (1:5515) (419), but *will* occur to a very small extent with cyclopentanone (1:5446) (421) or cyclohexanone (1:5465) (421) cf. (418).]

With amines. C̄ with primary amines in pres. of alc. caustic alkali condenses with loss of 3 HCl giving the corresp. isocyanides whose extremely characteristic odor has caused this general procedure to be used as a test (422) for primary amines. The reaction has, however, been very little studied in the aliphatic series.

[C̄ with CH_3NH_2 + alc. NaOH should give methyl isocyanide (methyl carbylamine) [Beil. IV-56, IV_1-(328), IV_2-(561)], b.p. 59.6° at 760 mm. (423), 59–60° (424), D_4^{20} = 0.734 (424), D_4^{20} = 0.7464 (425), n_{He}^{20} = 1.343 (424), but this highly explosive (425) (426) (427) substance has been reported only by other means, e.g., from MeI with dry AgCN (425) (423), CuCN (428), or CH_3HgI (429). — C̄ with $C_2H_5NH_2$ + alc. NaOH gives (430) ethyl isocyanide (ethyl carbylamine) [Beil. IV-107, IV_1-(351), IV_2-(600)], b.p. 78.1° at 760 mm. (431), 78° (424), D_4^{20} = 0.747 (424), D_4^{20} = 0.7405 (425), n_{He}^{20} = 1.362 (424), but this less explosive prod. (427) is usually obtd. by other means, e.g., from EtI with AgCN (425) (431), etc. — C̄ with *n*-$BuNH_2$ + aq. NaOH gives (only 5% yield (432)) *n*-butyl isocyanide (*n*-butyl carbylamine) which is better obtd. (40% yield (432)) from *n*-BuI + AgCN.]

[C̄ with aniline in alc. KOH (433) (435) cf. (438) or in C_6H_6 + $NaNH_2$ (436), or better in MeOH/NaOH (50% yield (434)) or powdered KOH without solvent (35–40% yield (437)) cf. (438), gives phenyl isocyanide (phenyl carbylamine) [Beil. XII-191, XII_1-(168)], b.p. 165–166° at ord. press. with partial polymerization (435), 78° at 40 mm. (435), 64° at 20 mm. (435), $D_4^{15.1}$ = 0.9823 (424), $n_{He}^{15.1}$ = 1.5282S (424). — For analogous reactions of C̄ with *o*-toluidine giving *o*-tolyl isocyanide [Beil. XII-788], b.p. 183–184° cor. at 753 mm. (439), with *p*-toluidine giving (440) (441) *p*-tolyl isocyanide [Beil. XII-903], b.p. 99° at 32 mm. (441), 94° at 25 mm. (434), m.p. 21° (441), 19.5° (434), with *p*-methoxyaniline (*p*-anisidine) giving *p*-methoxyphenyl isocyanide, m.p. 33° (438), 30° (434), with *o*-methoxyaniline (*o*-anisidine) giving *o*-methoxyphenyl isocyanide, b.p. 112° at 16 mm. (438), with *p*-phenylenediamine to give (442) either *p*-aminophenyl isocyanide, m.p. 74°, or *p*-phenylene diisocyanide see indic. refs. — Many other isocyanides are known but cannot be detailed here.]

Ⓟ Color reaction with α-naphthol/cyclohexanol. A. C̄ (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled 25 seconds and cooled, gives (174) blue color; one portion of this blue soln. underlaid with equal vol. of 85% H_2SO_4, stood 1 minute and shaken turns intensely blue; a second portion of the alkaline blue soln. acidified with equal vol. of AcOH (1:1010) stood 1 minute and shaken becomes orange-yellow. [Note that the alkaline boiling also gives a blue color with CH_2Cl_2 (3:5020) and with CCl_4 (3:5100) while other chlorinated solvents (174) give yellow-brown, gray, or brown; in the H_2SO_4 treatment CH_2Cl_2 (3:5020) gives greenish-blue and CCl_4 (3:5100) an intense blue; in the AcOH treatment CH_2Cl_2 (3:5020) gives a yellow, CCl_4 (3:5100) a red, color.]

B. $\bar{C}$ (1 drop) with 2 ml. cyclohexanol (1:6415) + a few mgms. α-naphthol (1:1500) + 2 ml. 20% aq. KOH boiled 15 seconds with vigorous shaking gives (175) blue color in upper layer. [Neither CH_2Cl_2 (3:5020) nor CCl_4 (3:5100) gives any color, and this form of the test may be used to detect as little as 1% $\bar{C}$ in either of the other two.]

Ⓟ **Color test with 2,7-dihydroxynaphthalene/cyclohexanol.** $\bar{C}$ (1 drop) with 2 ml. pure cyclohexanol (1:6415) + 1 pellet NaOH + a few mgms. 2,7-dihydroxynaphthalene htd. at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml. 96% EtOH, gives deep red color (175). [Note that under these conditions CH_2Cl_2 (3:5020) gives a steel-blue color while CCl_4 (3:5100) gives pale yellow-brown color (175).]

Ⓟ **Color test with cyclopentanol.** $\bar{C}$ (1 drop) in 1 ml. cyclopentanol (1:6412) + 1 pellet NaOH boiled for 25 seconds, then shaken vigorously for 35 seconds, then treated with 4 ml. 96% EtOH and shaken, gives with $\bar{C}$ only a pale citron-yellow color (175). [Note that in this test CH_2Cl_2 (3.5020) gives a deep red color which intensifies or turns reddish-brown upon addition of EtOH; CCl_4 (3:5100) gives an intense brown color.]

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3:5060 OXALYL (DI)CHLORIDE

O=C—Cl
|
O=C—Cl

$C_2O_2Cl_2$ Beil. II - 542; II_1-(234); II_2-(508)

B.P.		M.P.		
63.5-64° at 763 mm. (1)		−10.0° (3)	D_4^{20} = 1.4785 (3)	n_D^{20} = 1.4316 (3)
62.1-62.3°	(2)	−12.0° (1)	1.480 (4)	1.4301 (4)
61.1° at 743 mm.	(3)		$D_4^{13.4}$ = 1.4484 (4)	
60-61°	(4)		$D_4^{12.0}$ = 1.4888 (4)	$n_D^{12.9}$ = 1.43445 (4)
59-60°	(5)			1.43395 (4)

[*See also ethoxalyl chloride* (3:5025).]

Colorless liq. whose vapors strongly attack respiratory passages. — Solns. of $\bar{C}$ in ether, $CHCl_3$, or alkanes are colorless, but those in phenol, anisole, thioethers, piperonal, and dipentene are yellow (5). — Note that the presence in samples of $\bar{C}$ of phosphorous compds.

(such as might remain from the reagts. used in its prepn.) *increases* the refractive index (4); such contaminants may be removed by treatment with Cl_2 and subsequent fractionation (4) (7). — C̄ is stable to fumg. H_2SO_4.

C̄ is an important reagent in organic synthesis; its reactions may conveniently be classified under four main types, viz.: (*A*) those in which it reacts as an acid chloride (either one or both groups being involved); (*B*) those in which it acts like a mixture of $COCl_2$ (3:5000) + CO; (*C*) those in which it acts as a chlorinating agent; and (*D*) those in which it acts as a dehydrating agent. Examples of all these types will be found in the subsequent text, but naturally combinations of the distinctive types may occur simultaneously.

C̄ is also employed in the preparation of various dyestuffs although these cannot be discussed here. [For toxicity of C̄ see (6); for protection of stopcocks from action of C̄ see (16).]

Preparation. [For prepn. of C̄ from anhydrous oxalic acid (1:0535) with PCl_5 (2 moles) (yields: 70% (8), 45–50% (1)) in pres. of an inert solid or liq. diluent (9) and even in units as much as 5 times the original (10), or with PCl_3 in $POCl_3$ in stream of Cl_2 (11), or with $COCl_2$ (3:5000) in pres. of tertiary amines (14) see indic. refs.; from diethyl oxalate (1:1055) with PCl_5 (poor yields) see (12) (1) (13).]

[For prepn. of C̄ from $COCl_2$ (3:5000) + CO, or from CO + Cl_2 over suitable cat. at 200–400° and 200 atm. press., see (15).]

[For formn. of C̄ (19% yield (1)) from ethoxalyl chloride (3:5625) with PCl_5 in s.t. at 170° see (1).]

Pyrolysis or decomposition of C̄. [C̄ on passing through tube at 600° (1) or on htg. at 340° for 70 hrs. in an evacuated s.t. (7) dec. quant. into $COCl_2$ (3:5000) and CO; note, however, that at 200° C̄ shows no trace of phosgene even after 18 hrs. (7) and at ordinary temp. (when protected from light and moisture) can be preserved indefinitely.]

C̄ (1 mole) on slight warming with $AlCl_3$ (2 moles) in CS_2 dec. quant. (1) into phosgene (3:5000) + CO and may thus serve as a source of $COCl_2$ in Friedel-Crafts reactns. (see below).

C̄ when exposed to light of any wave length below 3800 Å slowly dec., the final prods. being $COCl_2$ (3:5000) + CO although the initial prods. appear to include Cl_2 and CO (16); this photochemical decn. plays an important part in its use as a reagent for introduction of the —CO.Cl group (chloroformylation) (see below).

Behavior of C̄ with inorganic reactants. C̄ with liq. aq. or dil. aq. alk. yields quant. (1) CO + CO_2 + HCl, no trace of oxalic acid (1:0445) or of its semi-acid chloride being formed; however, C̄ as vapor on treatment with steam does yield also some oxalic acid crystals (1).

[C̄ in ether on treatment with dry H_2S for several hrs. is unchanged, but if quinoline (2 moles) is added, vigorous reactn. occurs (1) with evolution of gaseous CO + COS.]

[C̄ on treatment with HBr gas for 12 hrs. gives (85% yield (7)) (17) (18) oxalyl (di)-bromide [Beil. II_1-(236), II_2-(509)], b.p. 106° (18), 102–103° at 720 mm., 16–17° at 10 mm., f.p. −19.5° (7) (for study of thermal and photochemical decn. of this prod. see (18)). — C̄ with HI is reduced (7) yielding CO + I_2 (cf. phosgene (3:5000)).]

C̄ with 2 NaI in *dry acetone* yields quant. (41) CO + I_2 + 2NACl but C̄ with aq. NaI does *not* set free iodine giving instead the usual aqueous hydrolysis with formn. of CO + CO_2 + 2HCl (41).

[C̄ (2 moles) with As_2O_3 (1 mole) gives (95% yield (19)) $AsCl_3$, b.p. 130°; similarly C̄ with dry CrO_3 refluxed 5 hrs. gives (80% yield (19)) chromyl chloride, CrO_2Cl_2, b.p. 114–116° at 748 mm.]

[C̄ in C_6H_6 with H_2 in pres. of $Pd/BaSO_4$ cat. gives only gaseous products, no trace of glyoxal or glyoxylic acid being formed (20).]

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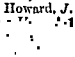
3:5060 OXALYL (DI)CHLORIDE



$C_2O_2Cl_2$

Beil. II - 542
II_1-(231)
II_2-(508)

B.P.		M.P.		
63.5-64° at 763 mm.	(1)	−10.0° (3)	D_4^{20} = 1.4785 (3)	n_D^{20} = 1.4316 (3)
62.1-62.3°	(2)	−12.0° (1)	1.480 (4)	1.4301 (4)
61.1° at 743 mm.	(3)		$D_4^{13.4}$ = 1.4484 (4)	
60-61°	(4)		$D_4^{12.0}$ = 1.4888 (4)	$n_D^{12.0}$ = 1.43145 (4)
59-60°	(5)			1.43395 (4)

[*See also ethoxalyl chloride* (3:5625).]

Colorless liq. whose vapors strongly attack respiratory passages. — Solns. of Č in ether, $CHCl_3$, or alkanes are colorless, but those in phenol, anisole, thioethers, piperonal, and dipentene are yellow (5). — Note that the presence in samples of Č of phosphorous compds.

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[Č in C_6H_6 with H_2 in pres. of $Pd/BaSO_4$ cat. gives only gaseous products, no trace of glyoxal or glyoxylic acid being formed (20).]

C̄ in C_6H_6 with NH_3 gas in cold reacts vigorously yielding (21) oxalic acid diamide (oxamide) [Beil. II-545, II_1-(237), II_2-(509)], m.p. above 400° (and therefore useless as derivative for identification), + NH_4Cl. — C̄ with hydrazine hydrate (excess) presumably yields oxalic acid dihydrazide ("oxalhydrazide") [Beil. II-559, II_1-(243), II_2-(514)], m.p. 244° dec., although this method of prepn. seems to be unreported.

[C̄ with K/Na alloy is (like many halogen compds.) sensitive to detonation by mechanical shock (GREAT DANGER) cf. (22). — For behavior of C̄ with other metals see (7).]

Behavior of C̄ with organic reactants. *Reaction of C̄ with alkanes and cycloalkanes.* [C̄ with satd. aliphatic hydrocarbons and with cycloparaffins in pres. of light and peroxides reacts to replace 1 H atom by the —CO.Cl group (22) (10); since this group represents the radical corresponding to the unisolatable acid chloride of formic acid, the process might well be designated as "chloroformylation"; however, since the resultant prods. may readily be hydrolyzed to the corresp. carboxylic acids, the process has also (unfortunately) been designated as "carboxylation." — E.g., C̄ (1 mole) with cyclohexane (1:8405) (2 moles) + dibenzoyl peroxide (0.005 mole) refluxed for 24 hrs. in light from low-press. Hg vapor lamp (10) or 300-watt tungsten lamp (23) gives (yields: 85% (23), 65% (10)) cyclohexanecarboxylic acid chloride (hexahydrobenzoyl chloride) (3:8580). — Note that neither simple olefins such as 2-methylbutene-2 (1:8220), octene-1 (1:8375), hexadecene-1 (cetene) (1:7000), nor cycloalkenes such as cyclohexene (1:8070) undergo this type of reactn. (24), although phenylethylene (styrene) (1:7435) gives cinnamoyl chloride (3:0330) (0% yield of cinnamic ac. after hydrolysis (24)) and phenylacetylene (1:7425) gives β-chlorocinnamoyl chloride (16% yield of β-chlorocinnamic acid after hydrolysis (24)). — Note also that C̄ under similar conditions with aralkyl hydrocarbons *chloroformylates the side chain but yields are very low (5–10%) (25).*]

Reactions of C̄ with aromatic hydrocarbons. [C̄ with aromatic hydrocarbons (R.H.) in pres. of $AlCl_3$ shows both (*A*) and (*B*) types of reactn. mentioned above in 2nd paragraph; on one hand (*A*) C̄ reacts like phosgene yielding R.CO.Cl (which during the usual subsequent treatment is hydrolyzed to the corresp. acid) and ketones of the type R_2CO; on the other (*B*) C̄ reacts with 2 PH as a bifunctional acid chloride yielding the corresp. 1,2-diketones, which with some of the polycyclic hydrocarbons comprise new cyclic systems of the quinone type. Examples of these various combinations are listed below.]

[C̄ with C_6H_6 + $AlCl_3$ in CS_2 gives according to mode of procedure either (1) 100% yield benzoyl chloride (3:6240) or 89% yield diphenyl ketone (benzophenone) (1:5150); note that no benzil (dibenzoyl) (1:9015) is formed here although it has been obtd. (in small proportion) together with benzophenone from oxalyl (di)bromide with C_6H_6 + $AlBr_3$ in CS_2 (17). — C̄ with toluene + $AlCl_3$ in CS_2 gives (65% yield (26)) *p*-toluic acid (1:0795). — C̄ with *o*-xylene (1:7430) + $AlCl_3$ in CS_2 gives (75–80% yield (27)) (26) 3,4-dimethylbenzoic acid [Beil. IX-535, IX_1-(210)], m.p. 166°, accompanied by some 3,4,3′,4′-tetramethylbenzil (4,4′-*o*-xylil), m.p. 128.5° cor. (27); C̄ with *m*-xylene (1:7420) similarly gives (40–50% yield (26)) 2,4-dimethylbenzoic acid [Beil. IX-531, IX_1-(209)], m.p. 126°; C̄ similarly with *p*-xylene (1:7415) gives (100% yield (26)) 2,5-dimethylbenzoic acid [Beil. IX-534, IX_1-(210)], m.p. 132°. — C̄ with ethylbenzene (1:7410) gives (29) *p*-ethylbenzoic acid [Beil. IX-529], m.p. 112°.]

[C̄ with arom. hydrocarbons contg. two uncondensed benzene nuclei shows a distinct tendency to yield dicarboxylic acids despite the fact that the first member is exceptional. E.g., C̄ with biphenyl (1:7175) + $AlCl_3$ in CS_2 gives (30) 40% yield di-*p*-xenyl ketone, m.p. 230°, + 25% *p*-xenil, m.p. 140–141°, although the formation in 75% yield of *p*-phenylbenzoic acid (*p*-xenoic acid) [Beil. IX-671, IX_1-(280)], m.p. 224°, has also been reported (31); for examples of dicarboxylic acid formn. from C̄ + $AlCl_3$ with 2,2′-dimethylbiphenyl (26), diphenylmethane (32), phenyl *p*-tolylmethane (26), di-*p*-tolylmethane (26), α,β-

diphenylethane (bibenzyl) (32), α,β-diphenylethylene (stilbene) (32), triphenylmethane (32), see indic. refs.]

[C̄ with polycyclic arom. hydrocarbons frequently, but not always, also gives polycyclic quinones; e.g., C̄ with naphthalene (1:7200) + $AlCl_3$ in CS_2 gives (35) a mixt. of α-naphthoic acid (1:0785) + β-naphthoic acid (1:0800); C̄ with 2-methylnaphthalene (1:7605) + $AlCl_3$ in CS_2 gives (33) a mixt. of acids + 2,2′-dimethylnaphthil + 3-methylacenaphthenequinone-1,2; for analogous results with 1,6-, 2,6-, and 2,7-dimethylnaphthalenes see (33) (34); C̄ with anthracene + $AlCl_3$ in CS_2 gives (70% yield (35)) aceanthrenequinone (1,9-oxalylanthracene) [Beil. VII_1-(436)], red pr. from C_6H_6, m.p. 270°, accompanied by some anthracene-9-carboxylic acid (*meso*-anthroic acid).]

[For behavior of C̄ + $AlCl_3$ with 2-methylanthracene (36) (38), 1,2-dibenzanthracene (37), retene or dihydroretene (39), or fluoranthene (40) see indic. refs.; many analogous cases are known but cannot be included here.]

Reaction of C̄ with alcohols and thiols. [C̄ with 2 moles primary alcs. especially in pres. of pyridine yields corresp neutral esters: e g., C̄ with MeOH (1:6120) (2 moles) gives dimethyl oxalate (1.0415), m.p. 54°; C̄ with EtOH (1:6130) (2 moles) gives diethyl oxalate (1.1055), b.p. 185°; for analogous behavior of C̄ with *n*-propyl alc. (1:6150) yielding di-*n*-propyl oxalate (1.3726), with isobutyl alc. (1:6165) yielding di-isobutyl oxalate (1:3897), with isoamyl alc. (1·6200) yielding diisoamyl oxalate (1:4181) all in 100% yield see (42). — C̄ with *secondary* alcs. (2 moles) also yields (42) (50) the corresp. neutral esters, but yields are less satisfactory and the ability of C̄ to act as a dehydrating agent begins to become evident (42); e.g., C̄ with methyl-phenyl-carbinol (1:6475) yields no ester, but only phenylethylene (styrene) (1:7435). — C̄ with *tertiary* alcs replaces OH by Cl; e.g., C̄ with *ter*-butyl alc. (1:6140) gives *ter*-butyl chloride (3:7045); C̄ with triphenylcarbinol (1:5985) gives chlorotriphenylmethane (3:3410) (42)]

[Note that C̄ with only 1 mole of primary alcs. yields the corresponding half esterification prods.; e g., C̄ (1 mole) with EtOH (1:6130) (1 mole) gives (60% yield (43)) ethoxalyl chloride (3 5625); for other examples together with use of such oxalic ester chlorides in prepn of cellulose esters see (43).]

[C̄ with ethylene glycol (1 6465) (1 mole) directly (42) or in pyridine (44) or in dry ether (45) gives (57% yield (45)) monomeric ethylene glycol oxalate (2,3-dioxodioxane-1,4) [Beil. XIX-153, XIX_1-(679)], m.p. 143° (45), 149° (44), 153° (42); for relationships of this monomer to the polymeric forms see (46).]

[C̄ with CH_3SH (2 moles) (13) in dry ether (47) gives dimethyl dithioloxalate [Beil. II-565, II_1-(514)], yel. cryst. from ether or lgr., m p. 82.5–83.5° (13), 80° (47), b.p. 218° at 760 mm. (47). — C̄ with EtSH (2 moles) (13) (48) in dry ether (1) gives diethyldithioloxalate [Beil. II-565, II_1-(244)], m.p. 27–27.5° (13), 24–25° (1), b.p. 238–240° at 757 mm. (1), 235° (13).]

Behavior of C̄ with phenols and thiophenols. [C̄ (1 mole) with phenol (2 moles) in dry ether with metallic Na (2 moles) gives (21% yield (49)) diphenyl oxalate [Beil. VI-155, VI_1-(87)], m p. 131° u c. (49). — C̄ (1 mole) with *o*-cresol (1:1400) (2 moles) + Na similarly gives (49) di-*o*-tolyl oxalate [Beil VI-355], ndls. from alc., m.p. 90–91° u.c. (49); C̄ with *m*-cresol (1 1730) similarly gives (49) di-*m*-tolyl oxalate [Beil. VI-379, VI_1-(187)], ndls. from alc , m.p. 105° u.c (49); C̄ with *p*-cresol (1:1410) similarly (49) or in pyridine (51) gives di-*p*-tolyl oxalate [Beil VI-398, VI_1-(201)], pl. from alc. + ether, m p. 148° (49), 147° (51), for similar behavior of still other phenols see (51)]

[Note, however, that C̄ (1 mole) with phenols (1 mole) in pres. of $AlCl_3$ leads to monoesterification followed by elimination of HCl and ring closure; e.g., C̄ (1 mole) with β-naphthol (1:1540) + $AlCl_3$ in CS_2 gives (85% yield (52) (53)) 4,5-benzocumarandione-2,3 [Beil. $XVII_1$-(267)], orange ndls. from AcOH, m p. 180–181° (52).]

[For behavior of C̄ with resorcinol (1:1530) + Na or K in moist ether see (54).]

[C̄ with β-thionaphthol (2-mercaptonaphthalene) + $AlCl_3$ in CS_2 esterifies and ring-closes with loss of HCl yielding (55) 4,5-benzothiocumarandione-2,3 (4,5-benzothionaphthenequinone-2,3), red pdr., m.p. 153°. — For extension of this type of reactn. to prepn. of halogenated thionaphthisatins from C̄ with halogenated 1- or 2-mercaptonaphthalenes + $AlCl_3$ see (56+).]

[For behavior of C̄ with dithiopyrocatechol (o-dimercaptobenzene) see (57).]

[For study of a series of molecular cpds. of C̄ with various hydroxy-azo compds. see (58).

Behavior of C̄ with phenol ethers. [C̄ with mononuclear phenol ethers + $AlCl_3$ reacts in general according to types *A* and *B* of paragraph 2 (above) so that after aqueous treatment involved in destroying the $AlCl_3$ there results either a diketone or a carboxylic acid; which of these is formed or their proportion varies with nature of components and with conditions. E.g., C̄ (1 mole) with anisole (methyl phenyl ether) (1:7445) (2 moles) + $AlCl_3$ (2 moles) in CS_2 gives (yields: 90% (59), 80% (60), 76% (17)) anisil (4,4′-dimethoxybenzil) [Beil. VIII-428, $VIII_1$-(705)], golden-yel. ndls. from alc., m.p. 133° (60), 132° (59); C̄ (1 mole) with phenetole (ethyl phenyl ether) (1:7485) (2 moles) + $AlCl_3$ in CS_2 gives (80% yield (29)) phenetil (4,4′-diethoxybenzil), pr. from ether + alc., m.p. 149°; C̄ similarly with o-cresol methyl ether (1:7480) + $AlCl_3$ in CS_2 gives (76% yield (61)) (59) 4,4′-dimethoxy-3,3′-dimethylbenzil, pale yel. ndls. from AcOH, toluene, or pyridine, m.p. 177° (61), 174° (59). — Note, however, that C̄ with *m*-cresol methyl ether (1:7510) + $AlCl_3$ in CS_2 yields no diketone, but only (59) 2-hydroxy-6-methylbenzoic acid (6-methylsalicylic acid) [Beil. X-217, X_1-(95)], m.p. 168°; C̄ with *p*-cresol methyl ether (1:7495) gives no diketone but only (12% yield (59)) 2-hydroxy-5-methylbenzoic acid (5-methylsalicylic acid) [Beil. X-227, X_1-(98)], m.p. 149° (59). — Many analogous cases of each type are known but cannot be included here.]

[C̄ with pyrocatechol dimethyl ether (veratrole) (1:7560) + $AlCl_3$ gives (60) 2,3,2′,3′-tetramethoxybenzophenone; C̄ with resorcinol dimethyl ether (1:7570) gives (60) 2,4,2′,4′-tetramethoxybenzophenone; C̄ with hydroquinone dimethyl ether (1:7160) gives (60) 2,5,2′,5′-tetramethoxybenzophenone, but C̄ with orcinol dimethyl ether (3,5-dimethoxytoluene) + $AlCl_3$ gives (29) by ring closure 6-methoxy-4-methylcoumarandione-2,3, m.p. 165° (29).]

Behavior of C̄ with organic acids or their derivatives. [C̄ with silver oxalate in dry ether does *not* yield the unknown oxalic anhydride but instead immediately evolves CO + CO_2 until all the salt has disappeared (1).]

[C̄ with organic acids, their salts, or their anhydrides, gives the corresp. acid chlorides in good yield (19); furthermore under appropriate conditions C̄ with aromatic acids gives good yields (50) of the corresp. arom. anhydrides; for numerous examples see indic. refs.]

Behavior of C̄ with amines or their derivatives. C̄ with primary or secondary amines (2 moles) reacts normally as a bifunctional acid chloride yielding corresp. *N*-substituted oxamides (see also below under Ⓓ's).

[Note, however, that with amine salts reaction takes a different course. — E.g., C̄ with aniline hydrochloride at 15° evolves HCl and gives (100% yield (62)) oxanilyl chloride, C_6H_5.NH.CO.CO.Cl [Beil. XII-283, XII_1-(206)], pr. from pet. ether, m.p. 82.5°; C̄ with α-naphthylamine.HCl in chlorobenzene at 15° similarly yields (12) *N*-(α-naphthyl)oxamidyl chloride, $C_{10}H_7$.NH.CO.CO.Cl, m.p. 86° (62); C̄ with β-naphthylamine HCl similarly yields (62) *N*-(β-naphthyl)oxamidyl chloride, ndls. from C_6H_6, m.p. 114–115° dec. (62). — Note that these prods. with condensing agents such as $AlCl_3$.$FeCl_3$ or H_2SO_4 ring-close with loss of HCl to yield homologs of isatin: e.g., *N*-(α-naphthyl)oxamidyl chloride + $AlCl_3$ at 80–85° for 8 hrs. gives (63) 6,7-benzoisatin [Beil. XXI-524, XXI_1-(414)] ("1,2-naphthisatin"), red ndls., m.p. 255°; *N*-(β-naphthyl)oxamidyl chloride with $AlCl_3$ in

nitrobenzene at 80° gives (75–80% yield (63)) 4,5-benzoisatin ("2,1-naphthisatin") [Beil. XXI-525, XXI_1-(415)], m.p. 252–253°.]

[Note, furthermore, that the above general synthesis of isatin homologs can be carried out starting with N-acylated arom. amines: e.g., $\bar{C}$ with Na salt of N-(p-toluenesulfonyl)-p-toluidide in CS_2 splits out NaCl giving (64) N-(p-toluenesulfonyl)-N-(p-tolyl)oxamidyl chloride, cryst. from C_6H_6, m.p. 91–93° (64); this prod. on htg. with $AlCl_3$ loses HCl and ring-closes to N-(p-toluenesulfonyl)-5-methylisatin, cryst. from AcOH or C_6H_6, m.p. 202–205°, hydrolysis of which by stdg. 1 day with conc H_2SO_4 yields (64) 5-methylisatin [Beil. XXI-509, XXI_1-(401)], red ndls. from aq. or alc., m.p. 187°.]

[For analogous reactn. of $\bar{C}$ with secondary arom amines and ring closure to N-substituted isatins see (65).]

[$\bar{C}$ with N,N-dimethylaniline gives various prods. according to conditions: $\bar{C}$ (1 mole) with dimethylaniline (2 moles) in dry ether in cold gives (100% yield (66)) (p-dimethylaminobenzoyl)formyl chloride, $(CH_3)_2N.C_6H_4.CO.CO.Cl$, stable only in soln. and on treatment with aq. giving (80% yield (66)) (p-dimethylaminobenzoyl)formic acid, golden-yel. lfts. from AcOH or MeOH, m.p. 186–187° dec., $\bar{C}$ (1 mole) with dimethylaniline (4 moles) in C_6H_6, stood 15 hrs. in cold, then heated gives tetramethyldiaminobenzil + the carbinol base of "Crystal Violet" (for many further details see (66)); for use of $\bar{C}$ in prepn. of "Crystal Violet" see (67).]

[$\bar{C}$ with o-aminothiophenol (80) or with its Zn salt (68) at 60–80° until reactn. begins, then htd. at 100° for 1 hr., gives (60% yield (68)) *bis*-2,2′-benzothiazolyl [Beil. XXVII-744, $XXVII_1$-(626)], m.p. 300.5° u.c. (68), 304° (80); similarly $\bar{C}$ with Zn salt of o-aminoselenophenol gives (69) *bis*-2,2′-benzoselenazolyl, m.p. 314° u c (69).]

Behavior of $\bar{C}$ with certain amides. [$\bar{C}$ with urea directly or in ether gives (8) (21) parabanic acid (N,N′-oxalylurea) [Beil. XXIV-449, $XXIV_1$-(401)], cryst. from alc., m p. 244°, accompanied by more or less oxaldiureide, insol, m p. 270–275° dec. (8). — $\bar{C}$ with N,N′-dimethylurea gives (70% yield (8)) N,N′-dimethylparabanic acid [Beil. XXIV-453, $XXIV_1$-(404)], m p. 154° (8). — $\bar{C}$ with N-phenylurea in ether refluxed 3 hrs. gives (88% yield (8)) N-phenylparabanic acid [Beil. XXIV-454, $XXIV_1$-(405)], lfts. from alc., m p 213–214° cor, after sintering at 208° (8). — $\bar{C}$ with N,N′-diphenylurea in ether gives (100% yield (8)) N,N′-diphenylparabanic acid [Beil. XXIV-455, $XXIV_1$-(405)], ndls. from alc., m p 202° cor., after prelim. sintering (8)]

[For examples of condensation of $\bar{C}$ with various other amides see (21) (70) (71) (73); with various amino acids see (72).]

Behavior of $\bar{C}$ with carbonyl compounds. [$\bar{C}$ with ketones often acts like PCl_5 by replacing the oxygen with 2 chlorine atoms with evolution of CO + CO_2· for many specific examples see (74); also note that $\bar{C}$ with xanthone (1:7275) gives (75) (76) xanthone dichloride; $\bar{C}$ with N-methyl- or N-phenylacridone gives (77) dichlorides.]

Behavior of $\bar{C}$ with organometallic compounds. [$\bar{C}$ with nickel carbonyl reacts according to equation $Ni(CO)_4 + (CO\,Cl)_2 \rightarrow NiCl_2 + 6CO$ (13) — $\bar{C}$ with Et_2Cd (from C_2H_5MgBr + $CdCl_2$) gives (27% yield (77)) 3-ethylhexanol-3-one-4 (diethyl-propionyl-carbinol) [Beil. I-841, I_2-(881)], b.p. 178–179° (78). — For interference of $\bar{C}$ with the Michler's ketone test for RMgX cpds. see (79).]

Ⓓ **Oxalyl (di)chloride/1,4-dioxane mol. cpd.:** ndls. or pr. from pet. ether, m.p. 67–68° (81). [From $\bar{C}$ with 5 wt. pts. dioxane-1,4 (1:6400) in 25 vols. pet. ether at −5° in stream of dry air or N_2; the 1:1 mol. cpd. ppts. in 71–78% yield (81). — Note that this prod. may with aniline be converted to oxanilide (see below) or may be dislvd. in excess stand. alk. and titrated back with stand. acid; furthermore, on stdg. in moist air, it is quant. converted to oxalic acid dihydrate (1:0445). — Note also that

under same conditions no ppt. results with acetyl chloride (3:7065), benzoyl chloride (3:6240), malonyl (di)chloride (3:9030), succinyl (di)chloride (3:6200), fumaryl (di)chloride (3:5875), *sym.*-phthaloyl (di)chloride (3:6900), *unsym.*-phthaloyl (di)-chloride (3:2395) or terephthaloyl (di)chloride (3:2205) (81).]

Ⓓ **Oxanilide** (oxalic acid dianilide): pl. from C_6H_6 or nitrobenzene m.p. 254° (21) 252–253° (71). [From $\bar{C}$ + aniline in cold ether or from $\bar{C}$ + aniline hydrochloride in boilg. C_6H_6 (21); note that by virtue of the relative insolubility of oxanilide and its easy quantitative formn. it is often employed as means for quant. detn. of $\bar{C}$ cf. (1). — Note also that the half reactn. prod. oxanilyl chloride m.p. 82.5° has been mentioned above in main text.]

—— **Oxal-*bis*-(*p*-toluidide)**: m.p. 268° (cf. 1:0445).

—— **Oxal-*bis*-(α-naphthalide)**: m.p. 234°.

—— **Oxal-*bis*-(β-naphthalide)**: m.p. 275°.

Ⓓ **Oxal-*bis*-(phenylhydrazide)**: cryst. from alc. or AcOH m.p. 278° (82). [From $\bar{C}$ (1 mole) in C_6H_6 with phenylhydrazine (4 moles) in dry ether (82).]

—— **Oxal-*bis*-(*p*-nitrophenylhydrazide)**: unreported.

—— **Oxal-*bis*-(2,4-dinitrophenylhydrazide)**: yel. cryst. from alc. m.p. 292° after darkening at about 270°. [Prepd. indirectly.]

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3:5075 METHYL CHLOROFORMATE $Cl.COOCH_3$ $C_2H_3O_2Cl$ Beil. III - 9
("Methyl chlorocarbonate") III_1-(5)
III_2-(9)

B.P. 72–73° at 767 mm.	(1)	$D_4^{20} = 1.2231$ (1)	$n_D^{20} = 1.38675$ (1)
71.4–72.4°	(2)		
71.2–71.5° at 733 mm.	(3)	$D_4^{15.9} = 1.2240$ (6)	
71.4° cor.	(4)		
71.0–71.5° at 750 mm.	(7)		
71–71.5°	(20)		
69° at 720 mm.	(5)		

[*See also ethyl chlorocarbonate* (3:7295).]

C̄ is colorless liquid with penetrating odor and strong lachrymatory properties.

[For prepn. of C̄ from carbonyl chloride (phosgene)(3:5000) with MeOH see (8) (9) (7) (4) (10) (20) (21); from methyl formate (1:1000) with Cl_2 see (11) (12) (chloromethyl chloroformate (3:5275) is also formed); from pentachloroethyl chloroformate [Beil. III-13, III_1-(6)] (13) or from *bis*-(trichloromethyl) oxalate [Beil. III-17] (14) or from methyl trichloromethyl carbonate [Beil. III-17 III_1-(8) III_2-(15)] (15) with MeOH see indic. refs.]

Pyrolysis of C̄. Unlike the case of ethyl chloroformate (3:7295) the pyrolysis of C̄ appears to have been little studied: in quinoline the decomposition temp. is given (16) (17) as 36°; presumably the decomposition yields MeCl (3:7005) + CO_2.

Reactions of the —COOMe group of C̄. C̄ is *not* readily decomposed by cold aq. (4) (11) (18) and can even be washed to remove alc.; C̄ on boilg. with aq. or dil. acid or dil. alk., however, is readily hydrolyzed yielding MeOH (1:6120) + CO_2 + HCl.

[C̄ with Cl_2 under various conditions (19) (20) (21) (22) (23) yields successively chloromethyl chloroformate (3:5275) dichloromethyl chloroformate (3:5315) and ultimately trichloromethyl chloroformate ("diphosgene") (3:5515).]

[C̄ (10% excess) with $MeHSO_4$ at 100° under reflux for 6–8 hrs. gives (100% yield (24))

3:5085 1,1,1-TRICHLOROETHANE $CH_3.CCl_3$ $C_2H_3Cl_3$ Beil. I - 85
(Methylchloroform) I_1—
I_2-(55)

B.P.			F.P.			
74.5°	at 767 mm.	(1)	−30.4°	(4)	D_4^{20} = 1.3492	n_D^{20} = 1.43838 (4)
74.9°	at 758.3 mm.	(2)	−32.2°	(8)		1.4384 (1)
74.1°	at 760 mm.	(3)	−32.7°	(9)		1.4379 (9)
74°		(9)	−32.96°	(21)		
73.9° cor.	at 760 mm.	(4)				
73.86–73.94° cor.		(5)				
73.8°		(6)				
74.1–74.5°	at 747.5 mm.	(7)				

Liquid. — [For f.p./compn. data on mixts. of C̄ with 2,2-dichloropropane (3:7140) or with pentachloroethane (3:5880) see (8); for extensive study of vap. press., heat capacity, and other thermodynamic props. see (21); for soly. of aq. in C̄ see (22).] [For use of C̄ as dry cleaning fluid see (10); for use of C̄ in dewaxing of oils see (11).] [For detn. of C̄ in air by thermal decompn. method see (23).]

[For prepn. of C̄ from 1,1-dichloroethane (ethylidene dichloride) (3:5035) by actn. of Cl_2 see (12) (13) (7); for manufacture of C̄ from 1,1-dichloroethylene (vinylidene dichloride) (3:5005) by cat. addn. of HCl see (14) (15).]

C̄ with $Ca(OH)_2$ at ord. temp. loses HCl yielding (16) 1,1-dichloroethylene (3:5005).

C̄ with aq. under specified conditions and catalyst hydrolyzes to yield (17) (18) AcOH, AcCl, or Ac_2O.

[For study of actn. of fluorine on C̄ see (19).]

C̄ with phenol + aq. NaOH gives (20) small yield of a mixt. of *o*-hydroxyacetophenone (1:1746) and *p*-hydroxyacetophenone (1:1527). [For impt. clarification of previous misapprehension of this reactn. see (20).]

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3:5100 CARBON TETRACHLORIDE (Tetrachloromethane) CCl_4 Beil. I - 64, I_1-(12), I_2-(22)

B.P.		
77.4°	at 774 mm.	(1)
77.2°	at 766 mm.	(2)
76.9°	at 760 mm.	(3) (20)
76.87°	at 749 mm.	(4)
76.83°	at 760 mm.	(83)
76.8°		(5) (87)
76.75°	at 760 mm.	(6) (7) (19)
76.74°	at 760 mm.	(8) (9)
76.71°	at 760 mm.	(10)
76.70–76.74°	at 760 mm.	(11)
76.7° u.c.	at 754 mm.	(12)
76.69°	at 760 mm.	(55)
76.686°	at 760 mm.	(13)
76.685°	at 760 mm.	(14)
76.66°	at 760 mm.	(15)
76.6°	at 760 mm.	(48)
76.58–76.60°	at 761 mm.	(16)
76.52°	at 760 mm.	(49)
76.5°	at 759 mm.	(17)
76.5° (18)	at 760 mm.	(19)
76.45–76.50°	at 760 mm.	(21)
76.4°		(50) (73)
76.22–76.38°	at 741 mm.	(22)
76.2°	at 746 mm.	(56)
76.1°	at 743 mm.	(23)
76°	at 733 mm.	(24)
75.55°	at 760 mm.	(19)
75.4°	at 760 mm.	(25) (19)
75.3–75.4°	at 729 mm.	(56)
75.2°	at 751.4 mm.	(26)
74.95°	at 720 mm.	(10)
74.4–74.5°	at 709 mm.	(30)
73.50°	at 687 mm.	(27)
72.0°	at 643.2 mm.	(2)
71.0°	at 663 mm.	(23)
65.0°	at 559 mm.	(23)
62.0°	at 506 mm.	(23)
60.0°	at 416 mm.	(2)
58.5°	at 443 mm.	(23)
59.5°	at 393.85 mm.	(2)
54.8°	at 386 mm.	(23)
50.0°	at 328 mm.	(23)

F.P.	
−22° (28)	(51)
−22.3°	(52)
−22.5°	(17) (29)
−22.6°	(30) (83)
−22.7°	(31)
−22.81°	(15)
−22.83°	(32)
−22.86°	(33) (34)
−22.87°	(35) (36)
−22.89°	(37)
−22.9°	(38) (39) (53)
−22.95°	(7) (40) (41) (42)
−22.968°	(87)
−23.0	(43) (44) (45) (153)
−23.4°	(46)
−23.5°	(47)

See also Notes 4, 5, and 6.

D_4^{30} = 1.57480	(7)
$n_D^{25.2}$ = 1.45767	(65)
1.45707	(65)
D_4^{25} = 1.5850	(54)
1.58472	(55)
1.58469	(22)
1.58447	(5)
1.58445	(13)
1.58443	(7)
1.58434	(56)
1.58426	(57)
1.58414	(58)
1.5835	(23) (59) (166)
n_D^{25} = 1.45930	(21)
1.45759	(13)
1.4574	(66)
1.45732	(67)
1.45724	(166)
1.4549	(68)
$n_D^{23.8}$ = 1.45786	(69)
D_4^{20} = 1.59472	(60)
1.5944	(11)
1.5942	(61)
1.59407	(7)
1.5940	(61) (62) (63)
1.5924	(64)
1.46023	(50)
n_D^{20} = 1.4630	(70)
1.461	(15)
1.46048	(11)
1.46044	(13)
1.46041	(10)
1.46040	(55)
1.46026	(165)
1.46023	(27)
D_4^{15} = 1.60370	(7)
1.6011	(23)

See also Note 7.

$n_D^{19.68}$ = 1.46094	(10)
$n_D^{16.80}$ = 1.46266	(10)
n_D^{15} = 1.46325	(168)
1.46305	(7)
1.4629	[illegible]

B.P. (*Cont.*)			
46.3°	at 282 mm. (23)	$n_D^{12.3}$ = 1.4656	(71)
42.0°	at 236 mm. (23)		
36.0°	at 170.95 mm. (2)	n_D^{12} = 1.4674	(71)
31.0°	at 149 mm. (23)		
25.0°	at 116 mm. (23)	$n_D^{11.19}$ = 1.46580	(10)
		$n_D^{10.5}$ = 1.4661	(10)

See also Notes 1, 2, and 3.

Note 1. For studies of vap. press. of C̄ over range −20° to +283° (72) and range +10.2 to 76.4° (73) see indic. refs.

Note 2. For studies of effect on b.p., vap. press., vapor density of very intensive drying see (74) (75) (76) (77) (79) (80).

Note 3. For study of detn. of b.p. range of C̄ as method of estimation of impurities see (81).

Note 4. For studies on effect of prior history of sample on detn. of f.p. of C̄ see (82) (52) (51).

Note 5. For studies of influence of high press. of f.p. see (41) (83).

Note 6. Solid C̄ has a transition point variously determined as follows: −47° (85) cf. (17), −47.55° (33), −47.63° (15), −47.66° (32) (36), −47.84° (39), −48.1° (47), −48.5° (86), −48.54° (87).

Note 7. For studies of density of C̄ over ranges −186° to −80° (88), 0° to 283° (crit. temp.) (72), and −18° to +60° (89) see indic. refs.

[*See also methylene (di)chloride* (3:5020) *and chloroform* (3:5050).]

MISCELLANEOUS PHYSICAL PROPERTIES OF C̄

Various Solubility Relations

With water. C̄ is only very slightly sol. aq. and is eas. volatile with steam; e.g., 100 g aq. at 0° dis. 0.097 g. C̄ (91), at 10° 0.083 g. (91), at 15° 0.081 g. (8), at 20° 0.080 g. (91), at 30° 0.077 g. (8), 0.085 g. (91); for study of salting-out effect of KCl or $MgSO_4$ see (92). — For studies of soly. of aq. in C̄ at 0° (93), 10° (94), 20° (94), 25° (93), and 30° (93) (94) see indic. refs.; for study of reciprocal soly. of C̄ + aq. see (95).

With various inorganic compounds. [For data on soly. in C̄ of H_2 (96), O_2 (97) (98), O_3 (99) (100), air (96), N_2 (at high pressure) (101), NO (107), NO_2 (102), N_2O (96), NH_3 (103), H_2S (103), SO_2 (96) (116), HCl (103) (104) (105) (106), HBr (106), Cl_2 (108) (109) (110), or CO_2 (111) (112) see indic. refs. — For data on soly. of I_2 in C̄ see (113) (121) (122) (123) (124) (125); for study of nature of I_2 solns. in C̄ see (114); for soly. of I_2 in CCl_4 vapor see (115). — For data on soly. of sulfur in C̄ see (128) (129) (130). — For data on soly. of $AlCl_3$ in C̄ see (135).]

With various organic compounds. [For data on soly. in C̄ of ethane (116), ethylene (116) under high press. (101), acetylene (116), dimethyl ether (117), CH_3Cl (117) (118), $COCl_2$ (119) (120) see indic. refs.]

Binary Systems Containing C̄

(See also azeotropes containing C̄)

C̄ with various inorganic compounds. *C̄ + Cl₂:* for f.p./compn. data and diag. (note that 5 different cpds. are formed) see (20) cf. (17) (126). — *C̄ + Br₂:* for f.p./compn. data and diag. (eutectic has f.p. about −47.6° and conts. about 82.7 mole % C̄ (38)) see (38) cf. (125). — *C̄ + I₂:* see above under soly. of I_2 in C̄. — *C̄ + I-Cl:* for f.p./compn. data and

diag. (series of solid solns.) see (31) cf. (127). — $\bar{C}$ + SO_2: for f.p./compn. data and diag see (131) — $\bar{C}$ + H_2S: for f.p./compn diag see (132). — $\bar{C}$ + N_2O_4: for f.p./compn data and diag. see (133) — $\bar{C}$ + PCl_5: for formn. of compd. $2PCl_5 \cdot CCl_4$ see (134). — $\bar{C}$ + PBr_5: for formn. of 2 cpds see (134). — $\bar{C}$ + $TiCl_4$: for f.p./compn. data and diag see (53); for b.p and liq vapor compn see (48)

$\bar{C}$ with org. cpds. of Order 1. $\bar{C}$ + *n-heptane* (1:8575): for study of ht. of mixing see (136); for n_D^{20}/compn see (165) — $\bar{C}$ + C_6H_6 (1:7400): for f.p./compn. data and diag see (137) (138) (90), for data on D_{20}^{20} (12), D_{23}^{23} (12), D_{25}^{25} (12), D_4^{25} (57) (140) (166), and D_{30}^{30} (141) versus compn see indic refs , for $n_D^{16.8}$ (142), n_D^{20} (10), or n_D^{25} (65) (68) (166) versus compn see indic refs ; for refractive indices at various wave lengths see (67); for data on b.p. at 720 mm (10), vap press. (2) (58) (10) (65) (143) (163), heat of mixing (141) (144), liq.-vapor equil (145), or study of distn through packed column (139) see indic refs. — $\bar{C}$ + *toluene* (1:7405): for data on vap press (4) (143), D_{20}^{20} (12) cf (4), D_4^{25} (166), n_D^{15} (146), and n_D^{25} (4) (166) see indic refs — $\bar{C}$ + *cyclohexane* (1:8405). for f.p./compn data (147), D_4^{20} (62), D_4^{25} (140) (58), n_D^{25} (140) see indic refs.

$\bar{C}$ + *MeOH* (1:6120): for D_4^{25} and n_4^{25}/compn see (151). — $\bar{C}$ + *EtOH* (1:6130): for vap. press data/compn see (148) (149); for D_4^{25} (59) (166) and n_D^{15} (167) or n_D^{25} (166) see indic refs — $\bar{C}$ + *n-PrOH* (1:6150): for n_D^{25}/compn see (66) — $\bar{C}$ + *n-BuOH* (1:6180): for n_D^{20}/compn see (165) — $\bar{C}$ + *isoAmOH* (1.6200): for D_4^{25} and n_4^{25} versus compn. see (166) — $\bar{C}$ + *cyclohexanol* (1:6415): for f.p./compn data see (150)

$\bar{C}$ + *diethyl ether* (1.6110): for data on f.p./compn. (152), D_4^{20} (62), D_4^{25} (166), and n_D^{25} (166) see indic refs. — $\bar{C}$ + *diisopropyl ether* (1.6125): for D_4^{20}/compn. see (62). — $\bar{C}$ + *dioxane-1,4* (1:6400) for D_4^{20}/compn. see (62). — $\bar{C}$ + *anisole* (1:7445): for f.p./compn. data and diag see (153) — $\bar{C}$ + *diphenyl ether* (1:7125): for f.p./compn. data and diag see (153)

$\bar{C}$ + *acetone* (1:5400): for f.p./compn. data and diags see (90) (147); for D_4^{20} (62), D_4^{25} (59), and n_D^{25} (166) versus compn see indic refs

$\bar{C}$ + *MeOAc* (1:3005): for D_4^{25} and n_D^{25} versus compn. see (166) — $\bar{C}$ + *EtOAc* (1:3015): for f.p./compn data and diag see (152); for data on vap. press. (65) (192), D_4^{25} (166), n_D^{20} (27), n_D^{25} (166) cf (65) versus compn. see indic. refs — $\bar{C}$ + *EtOBz* (1:3721): for D_4^{20} compn see (61) — $\bar{C}$ + *diethyl carbonate* (1:3150): for D_{25}^{25}/compn. see (5).

$\bar{C}$ with org cpds. of Order 2. $\bar{C}$ + *nitrobenzene*: for f.p./compn. data and diag. (eutectic, f.p. −31.5°, conts 81.5 wt. % $\bar{C}$ (44)) see (44) cf. (138); for D_-^{20}, D_-^{44}, and n_D^{20} versus compn. see (154) — $\bar{C}$ + *aniline*: for f.p./compn data (147) and D_4^{25}/compn (155) see indic. refs — $\bar{C}$ + *quinoline*: for D_4^{20}/compn. see (62)

$\bar{C}$ with org. cpds. of Order 3. $\bar{C}$ + CH_2Cl_2 (3:5020): for data on b.p., D_4^{20}, and liq.-vapor equilibria see (156) — $\bar{C}$ + $CHCl_3$ (3:5050): for f.p./compn data and diag. (eutectic, f.p. −81.1°, conts 49.4 wt % $\bar{C}$ (16)) (38) (147) (157) cf. (125) see indic. refs.; for D_4^{20}/compn. see (156) (158) cf. (12); for n_D^{25} compn. see (166); for b.p and liq.-vapor equil. see (156). — $\bar{C}$ + *1,1-dichloroethane* (3:5035): for b.p., D_4^{20}, and liq.-vapor equil. see (156). — $\bar{C}$ + *1,2-dichloroethane* (3:5130): for data on b.p. (49) (159), liq.-vapor equil (49) (159) (160), D_{20}^{20}/compn (49) see indic. refs. — $\bar{C}$ + *pentachloroethane* (3:5880): for f.p./compn. data and diag see (157) — $\bar{C}$ + *1,1,2,2-tetrachloroethylene* (3:5460): for f.p./compn. data (15), vap. press (3) and liq.-vapor equil. (3) see indic. refs. — $\bar{C}$ + *2,2-dichloropropane* (3:7140): for f.p./compn. data see (45). — $\bar{C}$ + *ter-butyl chloride* (3:7015): for f.p./compn. data and diags (complete series of solid solns.) see (47) (161) — $\bar{C}$ + *chlorobenzene* (3:7903): for D_4^{20}/compn see (61)

$\bar{C}$ with org. cpds. of higher orders. $\bar{C}$ + CBr_4: for extensive study of this system see (162); for D_4^{25}/compn see (54). — $\bar{C}$ + C_2H_5Br: for D_4^{20}/compn. see (158) — $\bar{C}$ + *1,2-dibromoethane*: for f.p./compn. data and diag see (138).

$\bar{C}$ + CHI_3: for f.p./compn. data see (45). — $\bar{C}$ + *EtI:* for vap. press., liq.-vapor equil, and $n_D^{25.2}$ see (65).

$\bar{C}$ + CS_2: for f.p./compn. data (147), study of distn. (164) (168), D_{20}^{20}/compn. (164), D_{25}^{25}/compn. (12), and n_D^{15}/compn. (168) see indic. refs.

Ternary Systems Containing $\bar{C}$

(See also azeotropes containing $\bar{C}$)

$\bar{C}$ + *MeOH* (1:6120) + *aq.*: for studies of phase relations (169) cf. (170) and colloidal character (171) see indic. refs. — $\bar{C}$ + *EtOH* (1:6130) + *aq.*: for data on soly. relations incl. density and refractive indices see (173) cf. (170). — $\bar{C}$ + *EtOH* (1:6130) + C_6H_6 (1:7400): for data on vap. press see (148) — $\bar{C}$ + *EtOH* (1:6130) + *glycerol* (1:6540): for study of soly. relations see (172). — $\bar{C}$ + *n-PrOH* (1:6150) + *aq.*: for data and diags. of soly. relations at 20°, and n_D^{25}/compn., see (66) cf. (170). — $\bar{C}$ + *AcOH* (1:1010) + C_6H_6 (1:7400): for data on density and n_D^{25} see (68); for vap. press. data see (2). — $\bar{C}$ + *toluene* (1:7405) + *1,2-dibromoethane:* for extensive study see (4) (174). — $\bar{C}$ + CH_2Cl_2 (3:5020) + $CHCl_3$ (3:5050): for f.p./compn. data (ternary eutectic, f.p. −111.4°, conts. 13 wt. % $\bar{C}$ + 60 wt. % CH_2Cl_2 + 27 wt. % $CHCl_3$) see (46).

Binary Azeotropes Containing $\bar{C}$

$\bar{C}$ + *MeOH* (1:6120): $\bar{C}$ forms with MeOH a const.-boilg. mixt., b.p. 55.70° at 760 mm., contg 79.44 wt. % = 44 5 mole % $\bar{C}$ (175), b.p 54.4° at 734 mm., contg. 77 wt. % $\bar{C}$ (176), b.p. 54.2° at 718 mm., contg. 79 wt. % $\bar{C}$ (176); cf. also (177) (178). — $\bar{C}$ + *EtOH* (1:6130): $\bar{C}$ forms with EtOH a const.-boilg. mixt., b.p. 64.95° (175), 65.08° (179) at 760 mm., contg. 84 15 wt. % = 61.3 mole % (175) $\bar{C}$; cf. also (180) (181); for effect of press. on this azeotrope see (182). — $\bar{C}$ + *n-PrOH* (1:6150): $\bar{C}$ forms with *n*-PrOH a const.-boilg. mixt., b.p. 72.8° (175), 73.1° (179) at 760 mm , contg. 88.5 wt. % = 75 mole % (175) $\bar{C}$; cf. also (183). — $\bar{C}$ + *isoPrOH* (1:6135): $\bar{C}$ forms with isopropyl alc. a const.-boilg. mixt., b.p. 67.5° (175), 68 95° (184), contg. about 82 wt. % (175) (184) = 64 mole % $\bar{C}$; cf. also (183) — $\bar{C}$ + *n-BuOH* (1:6180). $\bar{C}$ forms with *n*-butyl alc. a const.-boilg. mixt., b.p. 76 55° at 760 mm., contg. 97.5 wt. % $\bar{C}$ (179). — $\bar{C}$ + *isoBuOH* (1:6165): $\bar{C}$ forms with isobutyl alc. a const.-boilg mixt., b.p. 75.8° at 760 mm., contg. 94.5 wt. % = 89 mole % $\bar{C}$ (175) cf. (183) (186) — $\bar{C}$ + *ter-BuOH* (1:6140): $\bar{C}$ forms with *ter*-butyl alc. a const.-boilg. mixt., b.p. 69.5° (175), 70.5° (185) at 760 mm., contg 83 wt. % (175), 76 wt. % (185) $\bar{C}$. — $\bar{C}$ + *ter-AmOH* (1:6160): $\bar{C}$ forms with dimethyl-ethyl-carbinol a const.-boilg. mixt., b.p. about 76° at 760 mm., contg about 95 wt. % $\bar{C}$ (185). — $\bar{C}$ + *allyl alcohol* (1:6145): $\bar{C}$ forms with allyl alc. a const.-boilg mixt., b.p. 72.5°, contg. 79 5 mole % $\bar{C}$ (187).

$\bar{C}$ + *acetone* (1:5400): $\bar{C}$ forms with acetone a const.-boilg. mixt , b.p. 55.9° at 763 mm. (188), about 56° at 760 mm. (185), contg. about 11.5 wt. % (185) $\bar{C}$. — $\bar{C}$ + *methyl ethyl ketone* (1:5405): $\bar{C}$ with methyl ethyl ketone forms a const -boilg mixt., b.p. 73.8° at 760 mm., contg 71 wt. % = 53.4 mole % (175) $\bar{C}$.

$\bar{C}$ + *AcOH* (1:1010): $\bar{C}$ forms with AcOH a const.-boilg. mixt., b.p. about 77° at 760 mm., contg. about 97 wt. % $\bar{C}$ (189).

$\bar{C}$ + *EtOAc* (1:3015): $\bar{C}$ forms with ethyl acetate a const.-boilg. mixt , b.p. 74.75° at 760 mm. (175) (190), contg 57 wt. % $\bar{C}$ (190); b.p. 76.15° at 789.2 mm. contg. 55 6 mole % $\bar{C}$ (191); b.p. 71.56° at 685.0 mm. contg 58 2 mole % $\bar{C}$ (27); b p. 66 72° at 583.7 mm. contg. 60.75 mole % $\bar{C}$ (191); b p. 61.32° at 484.5 mm. contg. 63.75 mole % $\bar{C}$ (191); b.p. 55.22° at 385.2 mm. contg. 67 75 mole % $\bar{C}$ (191); b.p. 47.36° at 285 7 mm. contg. 72 6 mole % $\bar{C}$ (191): for study of thermodynamics of system see (193). — $\bar{C}$ + *methyl propionate* (1:3020): $\bar{C}$ forms with methyl propionate a const.-boilg. mixt., b.p. 75.5° at 760 mm.,

contg. 60 wt. % = 46 mole % (175); b p. 76° at 760 mm. contg. about 75 wt. % (194) C̄. — *C̄ + n-Pr formate* (1:3030): C̄ forms with n-propyl formate a const.-boilg. mixt, b.p. 74 6° at 760 mm., contg about 69 wt. % C̄ (184).

C̄ + nitromethane: C̄ forms with nitromethane a const.-boilg. mixt., b.p. 71.3° at 760 mm., contg about 83 wt. % C̄ (184) — *C̄ + 1,2-dichloroethane* (3:5130): C̄ forms with ethylene dichloride a const -boilg. mixt., b.p. 75.30° at 760 mm, contg. about 70 mole % C̄ (49) cf. (159); b.p. about 76° at 760 mm contg 79 wt. % C̄ (185).

Ternary Azeotropes Containing C̄

C̄ + EtOH (1:6130) + *aq :* this system forms a ternary two-phase const -boilg. mixt., b.p. 61.8° at 760 mm. (181) (175), contg. 86 3 wt. % = 57.6 mole % C̄ + 10.3 wt. % = 23.0 mole % EtOH + 3 4 wt. % = 19 4 mole % aq ; for use of this azeotrope in detn. of water content of wood see (195). — *C̄ + n-PrOH* (1·6150) + *aq :* this system forms a ternary two-phase const.-boilg mixt., b.p 54.4° at 760 mm., contg 54 4 mole % C̄ + 18 0 mole % n-propyl alc. + 27 6 mole % aq. (175). — *C̄ + allyl alc.* (1:6145) + *aq :* this system forms a const.-boilg mixt, b p. 65 4° at 760 mm, contg. 90.43 wt % = 64.5 mole % C̄ + 5.44 wt. % = 10 4 mole % allyl alc. + 4.13 wt. % = 25.1 mole % aq. (187); b.p. 65.15° at 760 mm contg 53 8 mole % C̄ + 18.7 mole % allyl alc. + 27.5 mole % aq (175). — *C̄ + ter-BuOH* (1.6140) + *aq :* this system forms a const -boilg mixt., b p 64.7° at 768 mm., contg about 85 wt % C̄ + 11.9 wt. % ter-BuOH + 3.1 wt % aq (188)

C̄ + methyl ethyl ketone (1:5405) + *aq :* this system gives a const -boilg. mixt., b.p. 65.7° at 760 mm, contg 76 9 wt. % C̄ + 20.1 wt. % methyl ethyl ketone + 3.0 wt. % aq. (188); for use of this azeotrope in detn of water in wood see (195).

Other Selected Physical Characteristics of C̄

[For studies of thermal conductivity of C̄ see (196) (197) (198); for studies of heat capacity of C̄ (39) (15) (183) as calcd. from spectroscopic data (199) (200) see indic. refs.; for studies of specific heat of C̄ see (21); for studies of heat of fusion and/or of transition see (39) (15) (36) (86) (157); for studies on ebullioscopic const. of C̄, viz., 4.88° (201), 4 68° (202) per mole solute in 1000 g C̄, see indic. refs.; for studies on cryoscopic const. of C̄, viz., 29.9° (203), 29 8° (204) per mole solute in 1000 g. C̄, see indic. refs.]

[For studies of adsorption of C̄ on various carbons (205) (206) (207) (208) (209) (210) (211) (212) (213) at low press. (214) (215), animal charcoal (216), wood or cocoanut charcoal (217) (218) (219) (220) (221) (222) (223) (224), alumina gel (225) (226), silica gel (227) (224) (228), $Fe(OH)_3$ gel (229) (230), $Cr(OH)_3$ gel (231), TiO_2 gel (232), or mica (233) see indic. refs.]

PHYSIOLOGICAL ASPECTS OF C̄

C̄ (as vapor) does not cause acute poisoning until exposure for 30 min. to concns. of 1000–1500 p.p.m. (234) but constant exposure to concns. above 100 p.p m. (234) (235) or even 50 p.p.m. (236) will cause serious physiological disturbances. The least concn. of C̄ in air detectable by odor is 71.8 p p.m. (237). For further studies of toxicity and industrial hygiene of C̄ see (238) (239) (240); for study of comparative toxicity of C̄ and 1,1,2-trichloroethylene (3:5170) see (241).

USES OF C̄

C̄ is widely used as solvent, fire extinguisher, *fumigant, anthelmintic, etc.;* although any detailed survey of these aspects is beyond the scope of this book, a few special uses are cited. [For study of use of C̄ as solvent for ozonization see (24); for use in concn. of HNO_3 (242)

or AcOH (243) or in drying of higher alcs. (244) see indic. refs.; for use of molecular compound (245) of $\bar{C}$ with rotenone in extraction (245) and detn. (246) (247) (248) of rotenone see indic. refs.]

DETECTION OR DETERMINATION OF $\bar{C}$

Detection of $\bar{C}$. [For detection of $\bar{C}$ in pres. of $CHCl_3$ (3:5050) q.v. by methods based on differences in aq. soly. (249), or on solv. power for papaverine HCl (250) or quinine sulfate (251), or on color reactions with pyrocatechol (1:1520) (252) (253), α-naphthol (1:1500) (254) cf. (255), or 2,7-dihydroxynaphthalene (255) cf. (254) (for further details on last two see at end of text of this compd. under Ⓟ), see indic. refs. For review of literature of tests for $\bar{C}$ see (256).]

Note that $\bar{C}$ does *not* (251) reduce Fehling soln. [dif. from $CHCl_3$ (3:5050)].

Determination of $\bar{C}$. Methods for the detn. of $\bar{C}$ are based upon both physical and chemical procedures or combinations of the two.

Physical methods include those based upon adsorption of $\bar{C}$, e.g., on activated carbon (257) or silica gel (258); by thermal conductivity of vapor of $\bar{C}$ (259); by measurement of vapor press. (260); or on interference refractrometry (234).

Chemical methods include those based upon decompn. of $\bar{C}$ by combustion and/or hydrolysis followed by detn. of HCl or of chloride ion, or those based upon color reactions. [For examples of methods based upon combustion followed by detn. of HCl (261) (262) (263) (264) (265) (266) (267) (268) (279) (for combustion in H_2 see (269)); methods based upon hydrolysis with alc. alk. (270) (271) (272) or reduction with Na + ethanolamine (273) (274) followed by detn. of chloride ion; or methods based upon use of color (Fujiwara) reaction with pyridine + alkali (275) (276) (277) (278) see indic. refs.]

DETECTION OF OTHER COMPOUNDS IN $\bar{C}$

[For studies on removal of $CHCl_3$ (3:5050) from $\bar{C}$ by digestion with Fehling soln. at 60–70° for several hrs. (280); on detection in $\bar{C}$ of CS_2 by addn. of MeOH (1:6120) and formn. of CS_2/MeOH azeotrope of b.p. 37.1° at 751 mm. (188) or by use of xanthate reaction (281); on removal of CS_2 from $\bar{C}$ by use of alc. hydrazine hydrate (282) see indic. refs.; for detection in $\bar{C}$ of carbonyl chloride see (283) (284) (285) (286) and also under phosgene (3:5000).]

PREPARATION OR FORMATION OF $\bar{C}$

The principal methods of prepn. of $\bar{C}$ are those involving chlorination of CS_2 or of hydrocarbons, but many other procedures have been studied as exemplified below.

From carbon disulfide. [Prepn. of $\bar{C}$ from CS_2 by action of Cl_2 was first effected (287) by passage through red-hot tube; in subsequent development of this method use of various catalysts has been found to reduce the required temperature. The overall reaction is believed to occur in two stages, viz., (1) $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ and (2) $CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$. The resultant sulfur may be recovered and used again in prepn. of CS_2.]

[For an extensive account of prepn. of $\bar{C}$ prior to 1906 see monograph of Margosches (288); for longer summary as of 1938 see (289); for still later patents and articles on use of Cl_2 (290) (291) (292) (293) (294) (295) or various sulfur chlorides (296) (297) (298) (299) see indic. refs.]

[For studies on use of various catalysts, e.g., Br_2 (300), I_2 (301), I_2 + Fe (302), $MoCl_5$ (303), $SbCl_5$ (304), or $FeCl_3$ (304), see indic. refs.; note that CS_2 reacts with $SbCl_5$ even without addn. of Cl_2 to give $\bar{C}$ (305).]

[Note that in chlorination of CS_2 with restricted amts. Cl_2 various intermediate carbon chlorosulfides have been detected (306) (307).]

From methane. The formation of $\bar{C}$, together with CH_3Cl (3:7005), CH_2Cl_2 (3:5020), $CHCl_3$ (3:5050), and other products, has been very extensively studied from many viewpoints. The literature of this reaction is diffuse and interlocked with that of methane and of the various other chlorination products. For this reason and because detailed treatment of this topic is beyond the scope of this book, the following citations must be regarded only as leading references.

[The formn. of $\bar{C}$ from CH_4 by action of Cl_2 was first discovered in 1840 by Dumas (308). For examples of more recent technical papers ((309)–(317), incl.) and patents ((318)–(332), incl.) see indic. refs.]

From other hydrocarbons. [For examples of patents on prepn. of $\bar{C}$ from aliph. hydrocarbons higher than methane (including in some cases also their halogen derivatives) see (313) (333) (334) (335) (336) (337). — For prepn. of $\bar{C}$ from acetylene + Cl_2 + cat. at 100–200° (338) or with Cl_2 + eutectic of $AlCl_3/NaCl/FeCl_3$ at 175–200° (339) see indic. refs. (see also below under prepn. of $\bar{C}$ from tetrachloroethylene). — For prepn. of $\bar{C}$ from naphthalene by destructive chlorination see (340).]

From various chloro and polychloro compounds. [For technical papers on prepn. of $\bar{C}$ from chlorinolysis of various chloro and polychloroparaffins (341) or chloropentanes (342) see indic. refs.]

[For patents on prepn. of $\bar{C}$ from tetrachloroethylene (3:5460) with Cl_2 at 700–800° (343) or with Cl_2 over activated carbon at 600–650° (337) see indic. refs.; for study of this reaction see (344). For formn. of $\bar{C}$ from hexachloroethane (3:4835) pyrolyzed in air at 550–600° see (342).]

[For prepn. of $\bar{C}$ from $CHCl_3$ (3:5050) by chlorination with Cl_2 in sunlight (first prepn. of $\bar{C}$) (345) or u.v. light (346) (347) (348) (349), at 260–300° (350), or in pres. of $FeCl_3$ (351) or of aq. (352), or from $CHCl_3$ with ICl at 165° (353), or with NaOCl (reaction very slow and incomplete (354)), see indic. refs.]

[For formn. of $\bar{C}$ from $CFCl_3$ with $AlCl_3$ see (355); from $CBrCl_3$ with Cl_2 in dark at 100° (356) or in light (357) (358) see indic. refs.]

From miscellaneous sources. [For formn. of $\bar{C}$ from charcoal or other form of carbon + Cl_2 see patents (359) (361) and technical papers (344) (360); from trichloroacetyl chloride (3:5420) on htg. with $AlCl_3$ (362) or pyrolysis through glass tube at 600° (363), from trichloromethyl chloroformate (3:5515) on htg. with $AlCl_3$ (364), from chloral (3:5210) with Cl_2 in sunlight (365), or from acetone (1:5400) with NaOCl soln. (366) cf. (354), or from phosgene (3:5000) on htg. with cat. (344) cf. (372), see indic. refs.]

[For formn. of $\bar{C}$ from dimethyl sulfide [Beil. I-288, I_1-(144), I_2-(276)] with Cl_2 + I_2 at 100–120° in daylight see (367) (368) (369); from trichloromethyl sulfur chloride ("perchloromethyl mercaptan") [Beil. III-135, III_1-(63), III_2-(106)] on htg. with Fe filings or ZnF_2 (370) cf. (307) (371) or with Cl_2 + I_2 in sunlight (370) see indic. refs.; from thiophosgene [Beil. III-134, III_1-(63), III_2-(105)] with Fe at 37° for many months or from "trichloromethyl dithiochloroformate" [Beil. III-215, III_2-(155)] with Fe in s.t. at 100° see (307).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$. [$\bar{C}$ on pyrolysis at 600–1500° (373) (374) cf. (344) (375) (376) gives tetrachloroethylene (3:5460) (80% yield (374)), hexachloroethane (3:4835), and other products. $\bar{C}$ by action of electric arc (377) cf. (378), dark electric discharge (in H_2) (379), radium emanation (380), gives hexachloroethane (3:4835) and various other products.]

[Note also that $\bar{C}$ in X-radiation (381) (382) or ultrasonic radiation (383) splits off some Cl_2. For action of X-radiation on mixts. of $\bar{C}$ with aq., $CHCl_3$, CHI_3, lgr., or cyclohexane see (381) (384); for decompn. of $\bar{C}$ in u.v. light below 2750 Å see (385).]

Oxidation of $\bar{C}$. $\bar{C}$ under various oxidizing conditions yields phosgene and other products. [E.g., $\bar{C}$ with O_2 in light of 2537 Å (386) or with atomic oxygen (387) gives carbonyl chloride (3:5000); $\bar{C}$ with O_2 over white-hot Pt (375), or with air over $CuCl_2$ or $FeCl_3$ at elev. temp. (388), or $\bar{C}$ over GeO_2 (389), or $\bar{C}$ with pyrosulfuryl chloride (1 mole) + sulfuric acid monohydrate (2 moles) on warming (390) (391) (392) (393) gives phosgene (3:5000). For formn. of phosgene (3:5000) q.v. during thermal decompn. of $\bar{C}$ (as in use as fire extinguisher) see (394), also below under behavior of $\bar{C}$ with metals.] [Note that $\bar{C}$, unlike $CHCl_3$ (3:5050), is *not* oxidized by Fehling soln.]

Reduction of $\bar{C}$. [$\bar{C}$ with K/Hg + aq. gives (395) methane; $\bar{C}$ with $Fe(OH)_2$ + aq. alk. gives (396) CH_2Cl_2 (3:5020) + $CHCl_3$ (3:5050); $\bar{C}$ with Zn + H_2SO_4 (397) (398), finely divided Fe + aq. (399) + cat. (400) (401), or on electrolytic reduction (402) gives $CHCl_3$ (3:5050). For behavior of $\bar{C}$ with atomic hydrogen see (403).]

[Note that $\bar{C}$ + H_2 over pumice in hot tube gives (404) $CHCl_3$ (3:5050), CH_2Cl_2 (3:5020), tetrachloroethylene (3:5460) + hexachloroethane (3:4835), and at red heat (395) methane and ethylene. $\bar{C}$ with excess H_2 over reduced Ni at 270° gives (405) hexachloroethane (3:4835) + HCl.]

Substitution of $\bar{C}$. $\bar{C}$ by reaction with F_2, metallic fluorides, or HF, etc., each in the presence of appropriate catalysts, undergoes replacement of one or more of its chlorine atoms by fluorine and consequent formation of mixed derivatives such as CCl_3F, CCl_2F_2 ("Freon" = "Freon-12" "F-12"), $CClF_3$, etc., to whose properties as refrigerants, etc., much attention is currently being given. [Detailed analysis of the conversion of $\bar{C}$ to these materials is far beyond the scope of this book, but for examples of leading technical papers (406) (407) (408) (409) (410) (411) and patents ((412)-(429)) see indic. refs.] (See also below under behavior of $\bar{C}$ with inorganic salts.)

Hydrolysis of $\bar{C}$. [$\bar{C}$ with aq. on long exposure (e.g., 7 months (430)) to sunlight gives CO_2 + HCl; $\bar{C}$ with large excess of aq. in s.t. at 250° also gives CO_2 + HCl, but $\bar{C}$ with very small proportion of aq. under same conditions gives (431) some phosgene (3:5000). At ord. temp. hydrolysis of $\bar{C}$ by pure aq. is scarcely perceptible, but in presence of Fe, Cu, acid, or alkali, hydrolysis is strongly accelerated especially at higher temperatures (432). $\bar{C}$ is hydrolyzed by aq. + reduced Fe but not by aq. $NaHCO_3$ (342) under reflux.]

[$\bar{C}$ with boilg. alc. alk. is eventually completely hydrolyzed (use in detn. of $\bar{C}$ by estimation of resultant chloride ion (see above)); however, reaction is slow and with *N* aq. or alc. KOH or NaOEt at 60° is very slight in 2 hrs. (433). For study of rate of hydrolysis of $\bar{C}$ with KOH in 95% alc. (434) cf. (435), or with $Ba(OH)_2$ or TlOH in 50% alc. (436), see indic. refs.]

Behavior of $\bar{C}$ with inorganic salts. [$\bar{C}$ with $AlBr_3$ at room temp. for 3 days gives (358) $CBrCl_3$ [Beil. I-67, I_2-(31)], b.p. 104.2–104.35° at 758.5 mm. (358), but $\bar{C}$ with $AlBr_3$ at 60° gives (437) cf. (438) CBr_4 [Beil. I-68, I_1-(17), I_2-(35)], m.p. 94°, b.p. 189.5° at 760 mm. with slight decompn. (439).]

[$\bar{C}$ with AlI_3 (440), Al + I_2 in CS_2 (441), CaI_2 + $2H_2O$ or LiI + $1.5H_2O$ in evacuated s.t. at 90–92° for 5 days (50–55% yield (442)) (443), with BI_3 (444), or $\bar{C}$ (1 mole) + C_2H_5I (4 moles) + $AlCl_3$ (0.1 mole) (445), or best $\bar{C}$ (0.7 mole) with CH_3I (2.94 moles) + $AlCl_3$ (0.015 mole) at 40° (92% yield (446)) gives carbon tetraiodide, CI_4 [Beil. I-74, I_1-(19), I_2-(39)].]

$\bar{C}$ with alc. $AgNO_3$ does not react even after several days; note that in this respect $\bar{C}$ behaves like CH_2Cl_2 (3:5020) and $CHCl_3$ (3:5050) while CH_3Cl (3:7005) gives a ppt. within 3 hrs. (446).

Behavior of $\bar{C}$ with metals. $\bar{C}$ with alkali or even alkaline-earth metals undergoes explosive decompn. on htg. or even at room temp. if subjected to sufficient mechanical shock. [For studies on the explosion of $\bar{C}$ with alkali metals see (477) (448); for further studies on explosion of $\bar{C}$ with Li, Na, K, Ca, Sr, Ba, Mg, Al, and Tl, expecially with reference to sensitivity to mechanical shock, see (449). — For behavior of $\bar{C}$ with Na vapor see (450); for rate of reaction of $\bar{C}$ with Na atoms see (451); for study of $\bar{C}$ + Na/Hg as means of sepn. of isotopes of chlorine see (452) cf. (453).]

[For study of hazards of behavior of $CCl_4/CHCl_3$ mixts. with Mg (454) (455) or Al (454) see indic. refs., note also that $\bar{C}$ refluxed with Al powder (456) or Al/Hg (457), or $\bar{C}$ with Al + $AlCl_3$ at 60–75° (458), or $\bar{C}$ with Cu powder at 120° (458) or molecular Ag at 200° (431) gives (yields. 80% (456), 65% (457)) hexachloroethane (3:4835).]

Note that $\bar{C}$ with Mg in boilg. ether does *not* react, even in the presence of various catalysts (459).

[For extensive study of corrosion of metals by $\bar{C}$ (460) cf. (461) (462) (463) (432) see indic. refs.]

Behavior of $\bar{C}$ with other inorganic reactants. [$\bar{C}$ is claimed to be unaffected by conc. H_2SO_4 at 237° (464) although over H_2SO_4 on pumice at 150° $\bar{C}$ is reported (465) to give HCl, SO_2, $COCl_2$ + CO_2.]

[For study of photochem. reaction of $\bar{C}$ with H_2S giving hexachloroethane (3:4835) + S + CCl_3SH see (466); for studies on photochem decompn. of Cl_2O in $\bar{C}$ see (467) (468) (469) (470) cf. (471); for behavior of $\bar{C}$ with Br_2O giving phosgene (3:5000) + Cl_2 + Br_2 see (472).]

[$\bar{C}$ with NH_3 under high press. in pres. of Cu + I_2 at 140° for 17 hrs. gives (35–40% yield (473)) guanidine hydrochloride [Beil. III 82, III_1-(39), III_2-(69)]. — $\bar{C}$ with hydrazine hydrate in stream of NH_3 refluxed for several days gives (poor yield (474)) N,N',N''-triaminoguanidine [Beil. III-122, III_1-(57), III_2-(97)], as monohydrochloride, m.p. 228° dec.]

Behavior of $\bar{C}$ with organic reactants. *With carbon monoxide.* [$\bar{C}$ with CO + $AlCl_3$ at 200° and 250 atm for 6 hrs gives (37% yield (475)) trichloroacetyl chloride (3:5420).]

With hydrocarbons. [$\bar{C}$ (excess) with octene-1 (1:8375) in pres. of small amts. (0.02 mole) of dibenzoyl peroxide (or diacetyl peroxide) adds to unsatd. linkage giving (476) 1,1,1,3-tetrachlorononane; under similar conditions $\bar{C}$ adds to one of the unsatd. linkages of diallyl (1:8045) giving *5,7,7,7-tetrachloroheptene-1 or to both giving* 1,1,1,3,6,8,8,8-octachloro-octane. — For other addns of $\bar{C}$ to olefin linkages see below.]

[$\bar{C}$ with C_6H_6 in pres. of $AlCl_3$ gives according to conditions triphenylchloromethane (3:3410) (477), triphenylmethane (1:7220) (478), or benzophenone (1:5150) (479). Other arom. hydrocarbons and aryl halides behave similarly but cannot be detailed here.]

With saturated halohydrocarbons. $\bar{C}$ (0.7 mole) with MeI (2.94 moles) + $AlCl_3$ (0.015 mole) at 40° gives (92% yield (446)) carbon tetraiodide (see also above under behavior of $\bar{C}$ with inorganic salts). — $\bar{C}$ with CBr_4 in pres. of slightly moistened $AlCl_3$ at 170° for 7 hrs. undergoes a redistribution reaction giving (480) an equil. mixt. of CCl_4, CCl_3Br, CCl_2Br_2, $CClBr_3$, and CBr_4.]

With unsaturated halohydrocarbons. [$\bar{C}$ with ord. 1,2-dichloroethylene (3:5030) + $AlCl_3$ gives (481) (482) cf. (483) 1,1,1,2,3,3-hexachloropropane (3:6460); for reaction of this system yielding heptachloropentenes see (483).]

[$\bar{C}$ with trichloroethylene (3:5170) + $AlCl_3$ at 20–30° for 48 hrs. gives (49% yield (484)) (481) (482) 1,1,1,2,3,3,3-heptachloropropane (3:6860).]

With alcohols or alcoholates. [$\bar{C}$ with MeOH over cat. at 200–350° gives (485) MeCl (3:7005); $\bar{C}$ with EtOH under similar circumstances gives EtCl (3:7015).]

[$\bar{C}$ with $NaOCH_3$ would be expected to yield tetramethyl orthocarbonate [Beil. III_2-(4)],

b.p. 112–113° at 724 mm. (486), n_D^{19} = 1.3841 (486), but this reaction is unreported, the expected prod. having been made only by other methods. — C̄ with $NaOC_2H_5$ would be expected to yield tetraethyl orthocarbonate [Beil. III-5, III_1-(4), III_2-(5)], b.p. 157–158° (487), 59.6–60° at 14 mm. (486), $D_4^{18.5}$ = 0.9197 (488), $n^{18.5}$ = 1.39354 (488), but this reaction is unreported cf. (505); however, the prod. has been prepd. from CBr_4 with NaOEt in dry ether in s.t. at 170° (487), from "thiocarbonyl tetrachloride," $CSCl_4$ cf. (489) refluxed in dry ether with NaOEt, and in other ways.]

With mercaptans or mercaptides. [C̄ with $NaSCH_3$ might be expected to give tetramethyl tetrathioorthocarbonate, $C(SCH_3)_4$, but this appears to be unreported; C̄ with $NaSCH_3$ has been found (492) to react differently giving trimethyl trithioorthoformate [Beil. II_1-(39)], m.p. 16° (493), b.p. 220° dec. (493), 103–104° at 12 mm. (492), 96° at 9 mm. (493), n_D^{15} = 1.5696 (492), and dimethyl disulfide, b.p. 39–41° at 18 mm. (492). — C̄ with $NaSC_2H_5$ is claimed (491) to give the expected homologous tetraethyl tetrathioorthocarbonate $C(SC_2H_5)_4$, but this material was not well characterized, and C̄ with $NaSC_2H_5$ has subsequently (492) been found to give triethyl trithioorthoformate [Beil. II-95, II_1-(39)], b.p. 235° dec. (493), 174° at 760 mm. (494), D_D^{20} = 1.053 (495), n_D^{15} = 1.5410 (492). — For behavior of C̄ with salts of *n*-propyl, *n*-butyl, and *ter*-butyl mercaptans see (492).]

With phenols or phenolates. [C̄ with phenol (1:1420) in pres. of $ZnCl_2$ + ZnO at 120° gives (496) diphenyl carbonate (1:2335), various dihydroxybenzophenones, and other products; for analogous study of C̄ with *o*-cresol (1:1400) see (497).]

[C̄ with K phenolate at 170° gives mainly (498) aurin (pararosolic acid) (4′,4″-dihydroxyfuchsone) [Beil. VIII-361, $VIII_1$-(671)]; for analogous behavior of C̄ with K *o*-cresolate and K *m*-cresolate see (498).]

With diacyl peroxides. [C̄ refluxed with di-*n*-butyryl peroxide for 17 hrs. gives (499) *n*-propyl chloride (3:7040) + hexachloroethane (3:4835) + ethyl *n*-butyrate (1:3127); C̄ refluxed similarly with di-*n*-isobutyryl peroxide gives (499) isopropyl chloride (3:7025) + hexachloroethane (3:4835) + ethyl isobutyrate (1:3095).]

[C̄ with di-α-naphthyl peroxide under reflux gives (500) CO_2, α-chloronaphthalene (3:6878), α-naphthoic acid (1:0785), and other products; C̄ with di-β-naphthyl peroxide under reflux gives (500) CO_2, β-chloronaphthalene (3:1285), β-naphthoic acid (1:0800), and other products.]

[C̄ with dibenzoyl peroxide under reflux gives (501) (502) (503) 4-(trichloromethyl)-benzoic acid, hexachloroethane (3:4835), phosgene (3:5000), chlorobenzene (3:7903), and other products; for study of kinetics of reaction see (504).]

With salts of enolic esters. [C̄ with diethyl sodio-malonate (505) (507) or with diethyl disodio-malonate (506) (507) (508) (509) gives the Na enolate of tetraethyl α,γ-dicarboxyglutaconate, $(C_2H_5OOC)_2C{=}CH{-}CH(COOC_2H_5)_2$ [Beil. II-876, II_1-(336), II_2-(710)], b.p. 208–210° at 23 mm. (510), 200–204° at 18 mm. (510); note that this product is also obtd. from $CHCl_3$ (3:5050) with diethyl sodio-malonate (505) (511) (512) (513) (514) (515) (516) (517).]

[C̄ with 4 moles of Na enolate of ethyl cyanoacetate in alc. at 100° gives (505) cf. (508) the sodium enolate of diethyl α,γ-dicyanoglutaconate, $C_2H_5OOC{-}C(CN){=}CH{-}CH(CN)COOC_2H_5$ [Beil. II-878, II_2-(712)], also obtd. from $CHCl_3$ (3:5050) with the Na enolate of ethyl cyanoacetate (518) (519) (520).]

With amines. The behavior of C̄ with amines has been little studied. [For studies on the behavior of C̄ with aniline (521) and also with other aromatic amines in pres. of Cu powder (522) or I_2 (523) see indic. refs.]

Ⓟ Color reaction with α-naphthol/cyclohexanol. C̄ (1 drop) with 2 ml. of a 2% soln. of α-naphthol (1:1500) in cyclohexanol (1:6415) + 1 pellet of solid NaOH, boiled

25 seconds and cooled, gives (254) blue color; one portion of this blue solution underlaid with equal volume 85% H_2SO_4, stood 1 min and shaken, remains blue; a second portion of the alkaline blue soln. acidified with equal vol. AcOH (1:1010), stood 1 min. and shaken, becomes red. [Note that the alkaline boilg. also gives a blue color with CH_2Cl_2 (3.5020) and with $CHCl_3$ (3:5050), while other chlorinated solvents (254) give yellow-brown, gray, or brown; in the H_2SO_4 acidification CH_2Cl_2 (3:5020) gives greenish blue, while both $CHCl_3$ (3.5050) and $\bar{C}$ give intense blue; in the AcOH acidification CH_2Cl_2 (3.5020) gives yellow while $CHCl_3$ (3:5050) gives an orange-yellow color.]

Ⓟ **Color test with 2,7-dihydroxynaphthalene/cyclohexanol.** $\bar{C}$ (1 drop) with 2 ml. pure cyclohexanol (1.6415) + 1 pellet NaOH + a few mgms 2,7-dihydroxynaphthalene htd at 197° (b.p. of ethylene glycol) for 45 seconds, decanted from undissolved NaOH, cooled, and shaken with 2 ml. AcOH + 4 ml 96% EtOH, gives a pale yellow-brown color (255). [Note that under these conditions CH_2Cl_2 (3.5020) gives a steel-blue color while $CHCl_3$ (3.5050) gives a deep red color.]

Ⓟ **Color test with cyclopentanol.** $\bar{C}$ (1 drop) in 1 ml. cyclopentanol (1:6412) + 1 pellet NaOH boiled 25 seconds, then shaken vigorously for 35 seconds, and treated with 4 ml. 96% EtOH and shaken, gives an intense brown color (255) [Note that, after addition of alc., CH_2Cl_2 (3:5020) gives a more intense red or becomes reddish brown while $CHCl_3$ (3 5050) gives only a pale citron-yellow. By comparing with authentic known samples, this test is claimed (255) to be able to detect as little as 5% $\bar{C}$ in $CHCl_3$.]

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3:5110 1,2-DICHLOROPROPENE-1 (Low-boilg. stereoisomer)

$CH_3—C(Cl)=CH(Cl)$ $C_3H_4Cl_2$ Beil. I - 199; I_1—; I_2—

B.P.

77.0° at 757.2 mm. (1)	D_4^{25} = **1.1755** (1)	n_D^{25} = **1.4451** (1)
75° (2)	D_4^{20} = **1.1818** (1)	n_D^{20} = **1.4471** (1)

[*See also the higher-boilg. stereoisomer* (3:5150).]

[For prepn. of Č from 1,2,2-trichloropropane (3:5475) with MeOH/NaOMe or EtOH NaOEt at ord. temp. (55–58% yield (1)), or with alc. KOH (2) or with aq. on htg. in s.t. (3), see indic. refs.]

Č with abs. MeOH (1:6120) forms a const.-boilg. mixt., b.p. 56.5–56.8° at 760 mm., n_D^{25} = 1.4030, contg. 75 wt. % Č (1).

Č with Cl_2 at 0° in strong light adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825).

C̄ with Br_2 at 0° slowly adds 1 mole halogen giving (1) (3) 1,2-dibromo-1,2-dichloropropane, b.p. 190° (3).

C̄ with O_3 in CCl_4 at −15° followed by aq. gives (1) acetic acid (1:1010) and formic acid (1:1005).

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3:5120 1,1-DICHLOROPROPENE-1 $CH_3.CH{=}CCl_2$ $C_3H_4Cl_2$ Beil. I-199
I₁—
I₂—

B.P. 79–80°	(1)	$D_0^{19.5} = 1.1764$ (8)
78°	(2) (3) (4) (5)	$D_0^0 = 1.2030$ (8)
77.15–77.35	(6)	
77°	(7)	
76.5°	(8)	

Colorless oil insol. in aq.

[For prepn. of C̄ from 1,1,1-trichloropropanol-2 (3:0846) with Zn dust + AcOH see (6) (5); from corresp. acetate with Zn dust + alc. see (8); from butylchloral (α,α,β-trichloro-n-butyraldehyde) (3:5910) (1) (2) (9) or its alcoholate (10) with KOH see indic. refs.; from Ag 2,2,3-trichlorobutyrate on boilg. with aq. (3) or Na 2,2,3-trichlorobutyrate on distn. (4) see (3) (4); for prepn. from 1,1,2-trichloropropane (3:5630) + aq. or alc. alk. or aq. $Ca(OH)_2$ see (11) (14).]

C̄ on oxidn. with $K_2Cr_2O_7 + H_2SO_4$ gives (7) AcOH (1:1010).

C̄ adds Br_2 very easily giving (9) 1,1-dichloro-1,2-dibromopropane [Beil. I-111], b.p. 188° (9). — C̄ with Cl_2 at 0–30° yields (12) 1,1,1,2-tetrachloropropane (3:5270), b.p. 153°.

C̄ with HCl + $AlCl_3$ at 5–10° yields (13) (14) 1,1,1-trichloropropane (ethylchloroform) (3:5270), b.p. 106–107°.

3:5120 (1) Krämer, Pinner, *Ber.* **3**, 388–389 (1870). (2) Krämer, Pinner, *Ann.* **158**, 47–49 (1871). (3) Judson, *Ber.* **3**, 789 (1870). (4) Valentin, *Ber.* **28**, 2663 (1895). (5) Wohl, Roth, *Ber.* **40**, 215 (1907). (6) Bruyne, Davis, Gross, *Physik Z.* **33**, 720 (1932). (7) Lieben, Zeisel, *Monatsh.* **4**, 536 (1883). (8) Faworski, Jozitsch, *J. Russ Phys.-Chem Soc.* **30**, 998–1003 (1898); *Cent.* **1899**, I 778 (9) Pinner, *Ann.* **179**, 44–45 (1875). (10) Freundler, *Bull. soc chim.* (4) **1**, 501–503 (1907).

(11) Cass (to du Pont), U.S. 2,134,102, Oct 25, 1938; Brit. 471,186, Sept 30, 1937. (12) Cass (to du Pont) U.S 2,097,442, Nov. 2, 1937; Brit. 471,187, Sept. 30, 1937; *Cent.* **1938**, 1218. (13) Levine, Cass (to du Pont), U.S. 2,179,218, Nov. 7, 1939; Brit 503,615, May 11, 1939; *Cent.* **1939**, II 1572. (14) Henne, Whaley, *J. Am. Chem. Soc.* **64**, 1157 (1942).

3:5130 1,2-DICHLOROETHANE (Ethylene (di)chloride; *sym.*-dichloroethane) CH_2—CH_2 (Cl, Cl) $C_2H_4Cl_2$ Beil. I - 84, I_1-(24), I_2-(52)

B.P.	F.P.		
84.1° cor. at 760 mm. (1)	[−32.5° (28)]	D_4^{25} = 1.2525 (40)	n_D^{25} = 1.4430 (47)
84.08° cor. at 760 mm. (2)	−35.3° (35)	1.2463 (41)	1.4427 (91)
84° at 760 mm. (3)	36° (11)	1.24571 (44)	1.4423 (14)
83.9° at 766 mm. (4)	−35.5° (23)	1.24554 (23)	1.44118 (48)
83.8° (5) (6)	(5)	1.2455 (42)	
83.75° at 760 mm. (7)	−35.8° (24)	1.2445 (43)	
83.7–84.3° (8)	−35.9° (37)	1.2444 (4)	
83.7–83.9° *cor. at 772 mm.* (9)	−36.0° (34) (38)		
83.7° at 760 mm. (10) (11) (12) (111) (112)	[−42.0° (39)]	D_4^{20} = 1.2569 (10) (22) (34)	n_D^{20} = 1.44507 (49)
			1.44505 (50)
83.65–83.70° at 760 mm. (13)		1.2541 (12)	1.44476 (18) (19) (20)
83.65° at 760 mm. (14)		1.25295 (44)	
83.6–83.8° (15) (16) (17)		1.25277 (23)	1.4447 (51)
83.5–83.7° (18) (19) (20)		1.2521 (45)	1.4446 (52) (79)
83.5° at 760 mm. (21) (22) (23) (34)		1.252 (3)	
		1.2515 (4)	1.4444 (53)
83.5° (24)		1.2501 (46)	1.44439 (46)
83.481° cor. at 760 mm. (25)			1.44432 (45)
83.45° at 760 mm. (26)			1.4443 (201)
83.43–83.48° (27)			1.4440 (54)
83.4–83.6° (28)			1.444 (34)
83.3° at 749 mm. (29)			1.44268 (13)
83° (30)			
82.85° at 760 mm. (100)		D_4^{15} = 1.26000 (23)	n_D^{15} = 1.44759 (23) See note 3.
82.6–82.8° at 743 mm. (31)			
82.4° at 747 mm. (32)			
82.3–82.6° (33)			
81.47° cor. at 700 mm. (2)			
79.325° cor. at 660.8 mm. (25)			
76.63° cor. at 600 mm. (2)			
75.05° cor. at 500 mm. (2)			
64.73° cor. at 400 mm. (2)			

See also Notes 1 and 2.

Note 1. For b.p. of $\bar{C}$ at press. 660–860 mm. (25), 400–1080 mm. (2), see indic. refs.; $\bar{C}$ has b.p. 84.9–85.5° at 777 mm. (53).

Note 2. For vap. press. of $\bar{C}$ over range −30 to 100° (1), or 0–30° (8), or 0–25° (55) see indic. refs.; for relation between vap. press. and temp. see (56) (25).

Note 3. For values of $n^{18.4}$ at 14 different wave lengths see (57).

Care must be taken to avoid confusion of $\bar{C}$ with either *cis* (3:5042) or *trans* (3:5028) 1,2-dichloroethylene.

MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relations. $\bar{C}$ is almost insol. aq., but easily volatile with steam (see under azeotropes); soly. of $\bar{C}$ in 100 g. aq at 0° is 0.873 g. (58), 0.922 g. (8); at 10° = 0.885 g. (8); at 15° = 0 872 g. (59), at 20° = 0.869 g. (8), 0.849 g. (58); at 25° = 0.865 g. (15); at 30° = 0.90 g. (59), 0.894 g. (8); at 35° = 0.895 g. (58); at 56° = 1.030 g. (58). — [For influence of added salts in diminishing soly. of $\bar{C}$ in aq. see (16). — Note that $\bar{C}$ with aq. under press. forms a solid hydrate which can be maintained up to +18° under 100 atm. but which at ord. press. decomposes below 0° (60). — For soly. of aq. in $\bar{C}$ at 0°, 25°, and 30° (as detd. by Karl Fischer reagt.) see (61).]

[For soly. in $\bar{C}$ of NH_3 at 20° and 1 atm. (62), of H_2S at 20° and 1 atm. (62), of HCl at various temps. and press. (62) (63), of ethylene at 0–40° (4), or of chlorine at −9° to +40° (4) see indic. refs.]

[For soly. in $\bar{C}$ of I_2 over range 11–25° (and comparison with other chlorinated solvents) see (64).]

[For study of industrial recovery of $\bar{C}$ by countercurrent absorption in kerosene see (65).]

Adsorption of $\bar{C}$ by solids. [For studies on adsorption of $\bar{C}$ by activated carbon (66) (67) (68) (69) (70), by silica gel (67), or by alumina gel (71) see indic. refs. — For patent on sepn. of $\bar{C}$ from other solvents by adsorption on carbon see (72).]

Other properties. [For study of thermal conductivity of $\bar{C}$ see (73); for study of diffusion of vapors of $\bar{C}$ through films of various cellulose esters see (74).]

Binary systems contg. $\bar{C}$. (See also azeotropes (below).)

$\bar{C}$ with hydrocarbons — *$\bar{C}$ + n-heptane* (1:8575): use in testing of distg columns (detn. of number of theoret. plates) see (75). — *$\bar{C}$ + cyclohexane* (1:8405): for values of D_0^{20} and n_D^{20} (49), for use in detn. of number of theoret. plates in distg. columns (75), or for sepn. of $\bar{C}$ from system by forming azeotrope of cyclohexane with MeOH (76), see indic. refs. (see also below under azeotropes).

$\bar{C}$ + benzene (1:7400): note that because of the proximity of the b.p.'s of the components, because of the importance of both as industrial solvents, and because they are *not* readily separable by chemical means (such as H_2SO_4, etc.) a great deal of study has been given to the system from various viewpoints.

For f p./compn. data on system $\bar{C}$ + C_6H_6, eutectic, f.p. −54.2°, contg. about 67 mole % $\bar{C}$ see (24) cf. (77); for D_{20}^{20} (78) (79), n_D^{20} (78) (79) (49), or $n_D^{25.2}$ (80) (89) cf. (81) see indic. refs — For use of this system as test liq. for studying efficiency of distn. columns see (81) (78) (79) (82), for study of distn. of the system see (78) (79) (81) (82) (83) (84) (85); for use in detn. number of theoret. plates see (75) (78); for data on vap. press. of system, vapor liq. compn., etc., see (86) (87) (88) (80) (49) (89) (90).

$\bar{C}$ + toluene (1:7405): for n_D^{25} for system see (91) (92); for vapor-liq. equil. data and study of distn. of system see (83) (91) (92) (93).

$\bar{C}$ with other cpds. of Order I. *$\bar{C}$ + acetic acid* (1:1010): for values of D and n for the system see (94), for vapor-liq. equil. see (95); see also under *uses* of $\bar{C}$ (below). — *$\bar{C}$ + phenol* (1:1420): for vap. press. of system see (96). — *$\bar{C}$ + acetone* (1:5400): for D and n_D^{20} see (49) (94), for vapor-liquid equil. see (49). — *$\bar{C}$ + diethyl ether* (1:6110): for f p./compn. data and diag. see (21); for D'_0 over range 0–40° see (97). — *$\bar{C}$ + ethylene oxide* (1:6105): for soly. and vap. press. (98) and vapor-liq. equil. (106) see indic. refs.

$\bar{C}$ with cpds. of Order III. *$\bar{C}$ + $CHCl_3$* (3:5050): for b.p./compn. diag. see (99). — *$\bar{C}$ + CCl_4* (3:5100): for D_{20}^{20} (100) and vapor-liq. compn. data and diagrams (100) (99) (88) (see also below under azeotropes).

$\bar{C}$ + 1,1-dichloroethane (3:5035): for b p at 760 mm., D_4^{20}, and vapor-liq. equil. data see (101). — *$\bar{C}$ + 1,1,2-trichloroethane* (3:5330): for f.p./compn. data, eutectic f.p. −79°

Note that oxidn. of $\bar{C}$ with CrO_3/H_2SO_4 in pres. of Hg yields CO_2 quantitatively (196) (dif. from many polychloro cpds.). — Note also that $\bar{C}$ does *not* respond to the R + H "Tri-Per Analyzer" (a recording ultra-violet photometer) (197).

For detn. of $\bar{C}$ in organs and tissues see (198).

PREPARATION OF $\bar{C}$

The most-studied method for prepn. and manufacture of $\bar{C}$ is that from ethylene by addn. of chlorine; this method is also of historical interest as leading to the discovery of $\bar{C}$ in 1795 (199) and its initial designation as "oil of the four Dutch chemists." — Various other modes of formn. of $\bar{C}$ have since been discovered and will be indicated below.

Preparation from ethylene. *By use of chlorine.* Ethylene with chlorine under certain conditions adds chlorine quant. yielding only $\bar{C}$; under other conditions, however, the system gives 1,1,2-trichloroethane (3:5330) + HCl. — In the absence of catalysts, the substitution reactn. is avoided by use of very low temperatures; in the presence of catalysts addition (rather than substitution) is facilitated even at the higher temperatures (e g., 120°) resulting from heat of reactn.

For general articles discussing the various factors involved see (200) (201) (53) (202) (203) (204) (205) (69); for articles discussing the reaction from the viewpoint of utilization of the ethylene of industrial gases see (206)–(214) incl.; for patents on prepn. of $\bar{C}$ from ethylene + Cl_2 see (215)–(236) incl. [For prepn. of "heavy" $\bar{C}$ contg. one C^{13} atom see below under miscell. prepns.]

By use of HOCl ($Cl_2 + H_2O$, etc.). Although ethylene with HOCl solns. gives mainly ethylene chlorohydrin (3:5552) nevertheless some $\bar{C}$ is formed; for studies of this reactn. see (237) (238) (239) (240) (241).

By other miscellaneous reagts. [For formn. of $\bar{C}$ (together with other prods.) from ethylene with Cl_2 in AcOH or Ac_2O soln. (242), with HCl + air over pumice contg. $CuCl_2$ at 300° (243), with aq. ICl (244), with NCl_3 in CCl_4 soln. at 20–25° for 7 days (245), with nitryl chloride ($ClNO_2$) (246), with $SbCl_5$ or $CuCl_2$ (247), or with *N*-chlorourea (253) see indic. refs.]

Formation of $\bar{C}$ from ethane or acetylene. [For formn. of $\bar{C}$ from ethane with NOCl at 300° (248) or with $Cl_2 + O_2$ + cat. at 300–650° (249) see indic. refs.; for formn. of $\bar{C}$ (together with other prods.) from acetylene with HCl gas in pres. of NO_2 (250), or with Cl_2 in pres. of $CCl_4 + AlCl_3/NaCl/FeCl_3$ at 175–250° (251) cf. (252), see indic. refs.]

Formation of $\bar{C}$ from miscellaneous sources and by various methods. [For formn. of $\bar{C}$ (together with other prods.) from methyl chloride (3:7005) in dark elec. discharge (254); from ethyl chloride (3:7015) with Cl_2 in light (255), with NCl_3 (256), or with $SbCl_5$ in s.t. at 100° (257); from 1,2-dibromoethane (ethylene dibromide) (1 mole) with $SbCl_5$ (2 moles) (note that use of only 1 mole $SbCl_5$ yields ethylene chlorobromide) (258); from 1-chloro-2-iodoethane (ethylene chloro-iodide) with finely divided Ag at 160° (259) see indic. refs.]

[For formn. of $\bar{C}$ (together with other prods.) from ethylene glycol (1:6465) with excess fumg. HCl in s.t. at 100° (260), with $PCl_3 + ZnCl_2$ (57% yield (261)), with PCl_5 (262), or $PCl_5 + ZnCl_2$ (37% yield (261)), with $SOCl_2$ + pyridine (62% yield (261)) see indic. refs.; from ethylene oxide (1:6105) with S_2Cl_2 (263); from 1,4-dioxane (1:6400) with Zn + acid chlorides (264); from 2-chloroethanol-1 (ethylene chlorohydrin) (3:5552) by disproportionation in s.t. at 184° for 10 hrs. (265) or during reactn. with HBr (266); from *bis*-(β-chloroethyl) sulfite with Cl_2 (267); from *bis*-(β-chloroethyl) sulfate with conc. aq. HCl (268) or with alk. chloride + dil. HCl (269) see indic. refs.]

[For formn. of $\bar{C}$ (together with other prods.) from diazomethane with $ZnCl_2$ in ether (270), from ethylenediamine with NOCl in xylene (271), see indic. refs.]

[For prepn. of "heavy" $\bar{C}$ contg. 1 C^{13} atom (from $NaC^{13}N$ via $CH_3C^{13}N$, $CH_3.C^{13}H_2NH_2$, $CH_3.C^{13}H_2N(CH_3)_3OH$, $CH_2{=}C^{13}H_2$) and its reactn. with Cl_2 see (272).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$. $\bar{C}$ on suitable htg. especially in pres. of dehydrohalogenating cat. loses 1 mole HCl yielding vinyl chloride (3:7010) [e.g., $\bar{C}$ over activated carbon at 230–250° (273), or with aq. vapor over cat. at 800–1000° (274), or over pumice at 600° (275) cf. (276) (277), or over alumina at low red heat (278) yields vinyl chloride (3·7010)].

Behavior of $\bar{C}$ with Inorganic Reactants

Reaction of $\bar{C}$ with Cl_2. $\bar{C}$ with Cl_2 gives according to the conditions chlorinated derivatives either of the ethylene or ethane series.

[E.g., $\bar{C}$ with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 400–480° gives (279) a mixt. contg. 20% 1,1-dichloroethylene (3:5005) + 22% 1,2-dichloroethylene (3:5030) + 29% trichloroethylene (3·5170) + 29% higher chlorination prods.; $\bar{C}$ with Cl_2 over suitable cat. at 300–500° gives (280) tetrachloroethylene (3:5460).]

[On the other hand, $\bar{C}$ with Cl_2 in ultra-violet light at 50° (281) (282), or 25° (283), or $\bar{C}$ with Cl_2 + suitable cat. at not above 60° (284), or $\bar{C}$ (as liquid) with Cl_2 (285), or $\bar{C}$ with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 300–425° as directed (279), or $\bar{C}$ with SO_2Cl_2 + trace of dibenzoyl peroxide refluxed 2 hrs. in dark (286) gives (yields: 80% (284), 70% (283) (286), 50% (279)) 1,1,2-trichloroethane (3:5330). — Furthermore, $\bar{C}$ with Cl_2 as directed (287) (288) or Cl_2 + $AlCl_3$ at 70–80° (289) (327) gives 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). — Finally $\bar{C}$ (in vapor phase) with Cl_2 + cat. (290) cf. (285) or $\bar{C}$ with Cl_2 at elev. temp. and press. (291) yields hexachloroethane (3:4835).]

Reaction of $\bar{C}$ with alkalies. $\bar{C}$ with alkalies or substances behaving as such may according to circumstances undergo either (or both) of two reactions: on the one hand $\bar{C}$ may lose HCl (1 mole) (dehydrohalogenation) yielding vinyl chloride (3:7010); on the other $\bar{C}$ may be hydrolyzed to ethylene glycol (1:6465).

Dehydrohalogenation. $\bar{C}$ with aq. alk. at elev. temp. and press. (292) especially in pres. of tetramethylene glycol, etc. (293), or $\bar{C}$ with MeOH/alk. (294), or EtOH/alk. (53) (295), loses HCl giving (91–93% yield (53)) vinyl chloride (3 7010). — [For study of rate of reactn. of $\bar{C}$ with KOH in 95% EtOH at 90° and 100° (296) (297), with NaOEt or KOEt in 95% EtOH or 48% EtOH at 90° (296) (297), or with MeOH/NaOMe at 17–19° (298) see indic. refs. — Note that $\bar{C}$ with alc. NaOEt at 100° under press. gives 90% yield (299) ethyl vinyl ether (1 7810).]

Hydrolysis. $\bar{C}$ under appropriate conditions hydrolyzes to ethylene glycol (1:6465); for general articles from this viewpoint see (110) (214) (314).

[For hydrolysis of $\bar{C}$ to ethylene glycol with aq. vapor over cat. at 550–850° (300), with aq. at 200° under press. in absence of any acid acceptor (301), or with aq. at 120° under press (302) see indic. refs. cf. (110).]

[For hydrolysis of $\bar{C}$ to ethylene glycol with aq. KOH at elevated temp. and press. see (110). — For study of use of Na_2CO_3 and/or $NaHCO_3$ in aq. (214) (303) (304) (305) (306) or in 85% EtOH (307) cf. (214) see indic. refs. — For use of aq. $CaCO_3$ in pres. of NH_4 salts (308) (309), or aq. $BaCO_3$ (310) at elev. temp. and press., see indic. refs. — For use of sodium formate in MeOH at 165° under press. (311) cf. (214), aq. + PbO in s.t. at 170° (312), or Fe_2O_3 (?) (313) see indic. refs.]

For use of hydrolysis with alk. followed by $KMnO_4$ oxidn. of resultant ethylene glycol to oxalic acid as means of distinction between $\bar{C}$ and the isomeric 1,1-dichloroethane (3:5035) see (256).

[For prepn. of "heavy" ... actn. of C̄ with aq. 2,4-dichlorophenol (3:0560) or with 2,4,6-tri-
H_2NH_2, $CH_3C^{13}H_2N(C73)$ at 73–98° for 24–66 hrs. giving respectively 1,2-*bis*-(2,4-dichloro-
m.p. 132–133°, and 1,2-*bis*-(2,4,6-trichlorophenoxy)ethane, m.p. 167–

of C̄ with 50% NaOH + cellulose see (358). — C̄ with MeOH over Al_2O_3
Pyrolysis of C̄. ... HCl yielding (359) vinyl chloride (3:7010) + MeCl (3:7005).]
1 mole HCl yiel... h. of "heavy" C̄, viz., $ClCH_2C^{13}H_2Cl$, with "heavy" benzyl mercaptan,
(273), or with $CH_2S^{34}H$, see (272).]
(276) (277). ... on of C̄ with salts of organic acids. C̄ with salts of acids yields the corresp. ethylene
...sters; note, however, that reactn. of only 1 chlorine atom can lead to β-chloroethyl
and that loss of HCl and subsequent formn. of vinyl esters (or their polymers) can
React... imes occur.
tives e.g., C̄ with NaCN yields (360) succino(di)nitrile [Beil. II-615, II_1-(265), II_2-(554)],
[E.g. 53–54° (for rate of reactn. of C̄ with alc KCN see (296)). — C̄ with anhydrous alkali
20% alk.-earth acetate at 230° in glycol diacetate (361) or monoacetate (364), or in alc. at
chl... 0–180° under press (362), or in pres. of an amine salt as cat. at 175–225° (363), yields
cat. ... thylene glycol diacetate (1:3511), b.p. 190°.]

Reaction of C̄ with miscellaneous non-nitrogenous org. cpds. [For reactn. of C̄ +
C̄ with ... Cl_3 (in CCl_4) with CO at 60–70° and 60–70 atm. press. yielding a mixt. of acid chlorides,
with C... ones, etc., see (365). — For reactn. of C̄ with CS_2 + aq. KOH yielding ethylene glycol
trace of ... thiocarbonate see (366)]

C̄ (0.5 mole) + ethylene dibromide (0.5 mole) + $AlCl_3$ (0.015 mole) refluxed 2 hrs.
(283) ... 7) or stood at 25° for 35 hrs. (368) undergoes a redistribution reaction giving a prod.
directed ... tg. 49.8 mole % 1-bromo-2-chloroethane (ethylene chlorobromide) [Beil. I-89, I_1-(28),
(acetyl... (61)], b.p. 107–108°, n_D^{20} = 1.4908 (369) — Similarly C̄ (1 mole) + ethyl bromide
of (283) ... moles) + $AlCl_3$ (3%) in steel bomb at 25° for 14 days gives a mixt. contg. five prods.
React... mole % as follows. C̄ 9%, EtCl 34%, ethylene chlorobromide 18%, ethylene dibromide
cording ... %, and EtBr 29% (367)]
may be ... For reactn. of C̄ with diethyl sodio-malonate leading to tetraethyl butane-1,1,4,4-
other C̄ ... racarboxylate [Beil. II-862, II_1-(333), II_2-(702)] together with various other prods. see
Dehyd... 0) (371).]

of tetra... **reactn. of C̄ with amines.** C̄ with aniline (4 moles) boiled ¾ hr. yields (372) *N,N'*-
loses HCl ... henyl-ethylenediamine (1,2-*bis*-(phenylaminoethane)) [Beil. XII-543, XII_1-(282)],
reactn. of ... 4° (373) (corresp. *bis*-acetyl deriv. m.p. 158°), probably accompanied by some *N,N'*-
95% ... ylpiperazine [Beil. XXIII-8, $XXIII_1$-(5)], m.p. 164°. [For nitration of 1,2-*bis*-
... ylaminoethane) see (372) (373); for nitration of *N,N'*-diphenylpiperazine see (374). —
... that C̄ with $NaNHC_6H_5$ (from aniline + $NaNH_2$ in dry ether) loses 2 HCl yielding
... acetylene.]

... with 33% abs. alc. Me_3N stood 10 days gives (22.5% yield (376)) the corresp. mono-
... ternary salt, β-chloroethyl-trimethyl-ammonium chloride ("choline dichloride");
... study of rate of reactn. of C̄ with Me_3N in 90% acetone at 55° see (377). — For studies
... rate of reactn. of C̄ with other amines, e.g., with benzylamine (296) (297), piperidine
... 96) (297) (298), pyridine (298) (378), see indic. refs.]

COLOR REACTIONS OF C̄

... With Weber reagent. C̄ (2 drops) with 2% soln. of phenolphthalein in cyclohexanol
(2 ml.) + trace solid NaOH htd. 5 min. at 190–200° (preferably in bath as directed (379)),
... then cooled and acidified with AcOH (1 ml.) gives lilac color. [Note that acetylene tetra-
... chloride (3:5750) with this reagt. gives a somewhat similar result.]

Comment on $NH_4OH/CuCl$ reagt. Note that C̄ with $NH_4OH/CuCl$ does *not* (380) give any color (dif. from 1,1-dichloroethane (ethylidene (di)chloride) (3:5035) which in 10 min. gives cloudy amethyst coloration (380)).

Comment on Fehling's soln. Note that C̄ does not reduce Fehling's soln. even on htg. (dif. from ethylidene (di)chloride (3:5035)).

Ⓓ **1,2-Diphenoxyethane** (ethylene glycol diphenyl ether) (1:7235). Lfts. from alc., m.p. 98°. [From C̄ with aq. K phenolate refluxed 48 hrs. (70–85% yield (353)); note, however, that if only one of the two chlorine atoms reacts some β-chloroethyl phenyl ether, m.p. 28°, b.p. 217–220° at 760 mm. (355), may be formed.]

—— **1,2-Di-α-naphthoxyethane** (ethylene glycol di-α-naphthyl ether) [Beil. VI-607]. Lfts. from alc., m.p. 127.5° (381). [From C̄ + α-naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). — Note that the half reactn. prod., β-chloroethyl α-naphthyl ether, has m.p. 28° (355).]

—— **1,2-Di-β-naphthoxyethane** (ethylene glycol di-β-naphthyl ether) [Beil. VI-642]. Lfts. from C_6H_6, m.p. 217° (381). [From C̄ + β-naphthol + aq. NaOH at 120° in s.t. for 8 hrs. (381). — Note that the half reactn. prod., β-chloroethyl β-naphthyl ether, has m.p. 83° (355).]

Ⓓ **Ethylene 1,2-bis-(isothiourea picrate):** ndls. from alc., m.p. 260° (382), 259° (332). [From C̄ with thiourea refluxed in alc. and subsequently treated with PkOH (332).]

Ⓓ **1,2-Diphthalimidoethane** (ethylene diphthalimide) [Beil. XXI-492, XXI_1-(384)]. Ndls. from AcOH, dil. AcOH or alc., m.p. 236° (383), 232–233° (384), 232° (385). [From C̄ + K phthalimide (2 moles) in s.t. at 200° (386); note that C̄ in very large excess with K phthalimide in s.t. at 180–190° for 3 hrs. gives (387) the half reactn. prod., *N*-(β-chloroethyl)phthalimide, cryst. from CS_2 or alc., m.p. 81° (388), 79–81° (387) (389).]

—— **1,2-Disaccharinoethane:** m.p. 253–254° (392). [Not reported from C̄ itself, but obtd. (20% yield) from ethylene (di)bromide with sodium saccharin in aq. butyl-carbitol (1:6517) contg. KI on refluxing for 3 hrs.; note that with shorter reflux (1 hr.) some half reactn. prod., viz., *N*-(β-bromoethyl)saccharin, m.p. 99°, is formed (392).]

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[illegible] Reymann (to Shell Dev. Co.).

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(231) Damiens, de Loisy, Piette, French 535,210, April 11, 1922; *Cent.* **1923**, II 741; not in *C.A.* (232) T. Goldschmidt, A. G., French 533,296, Feb. 27, 1922; *Cent.* **1922**, IV 393; not in *C.A.*: Brit. 147,909, Nov. 3, 1921; *Cent.* **1922**, IV 393–394; *C.A.* **15**, 97 (1921). (233) Goldschmidt, Arnold, Brit. 158,836, March 10, 1921; *Cent.* **1921**, II 1060; *C.A.* **15**, 1953 (1921). (234) Marks, Brit. *136,489, July 2, 1919; C.A.* **14**, *1122 (1920)*; not in *Cent.* (235) Harding, Brit. 126,511, June 11, 1918; *C.A.* **13**, 2375 (1919); not in *Cent.* (236) Gosudarstvennui Trest Rezinovoi Promuishlennosti & Matisen, Russian 24,877, Jan. 31, 1932; *Cent.* **1933**, I 672; *C.A.* **30**, 1808 (1936); also **26**, 3513 (1932). (237) Gomberg, *J. Am. Chem. Soc.* **41**, 1414–1431 (1919). (238) Shilov, Kanyaev, Domina, Ionina, *J. Phys. Chem.* (*U.S.S.R.*) **13**, 1242–1248 (1939); *C.A.* **35**, 371 (1941). (239) Shilov, Solodushenkov, Kurakin, *J. Phys. Chem.* (*U.S.S.R.*) **13**, 759–766 (1939); *C.A.* **34**, 7708 (1940). (240) Soc. Anon. Ind. Chim. Barzaghi, Italian 337,801, May 20, 1935; *Cent.* **1937**, I 3548; not in *C.A.*

(241) Irvine, Haworth (to Carbide and Carbon Chem. Corp.), U.S. 1,496,675, June 3, 1924; *Cent.* **1924**, II 1511; [*C.A.* **18**, 2345 (1924)]. (242) Weber, Hennion, Vogt, *J. Am. Chem. Soc.* **61**, 1457–1458 (1939). (243) Ernst, Wahl (to I. G.), Ger. 430,539, June 23, 1926; *Cent.* **1926**, II 1189; not in *C.A.* (244) Vorhees, Skinner, *J. Am. Chem. Soc.* **47**, 1127 (1925). (245) Coleman, Mullins, Pickering, *J. Am. Chem. Soc.* **50**, 2739–2741 (1928). (246) Steinkopf, Kühnel, *Ber.* **75**, 1323 (1942). (247) Wohler, *Ann. Physik.* **13**, 297 (1825/9). (248) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; *Cent.* **1939**, II 1775; *C.A.* **33**, 5001 (1939). (249) Gremli, Austrian 108,421, 108,424, Dec. 27, 1927; *Cent.* **1928**, I 1229; not in *C.A.* (250) Bauer (to Röhm,

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(261) Clark, Streight, *Trans. Roy. Soc. Canada* (3) **23**, III 77–89 (1929). (262) Wurtz, *Compt. rend.* **45**, 228 (1857); *Ann.* **104**, 174–175 (1857); *Ann. chim.* (3) **55**, 419–421 (1859). (263)

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(271) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30**, 606–632 (1898); *Cent.* **1899**, I 25. (272) Kilmer, du Vigneaud, *J. Biol. Chem.* **154**, 247–253 (1944). (273) I.G., Ger. 585,793, Oct. 9, 1933; *Cent.* **1934**, I 124; *C.A.* **28**, 1361 (1934). (274) Baxter, Edwards, Winter (to Imperial Chem. Ind., Ltd.), Brit. 363,009, Jan. 7, 1932; *Cent.* **1932**, I 3497; [*C.A.* **27**, 1365 (1933)]; French 721,808, Aug. 20, 1931; *C.A.* **26**, 4067 (1932). (275) Böeseken, Bastet, *Rec. trav. chim.* **32**, 187–188 (1913). (276) Biltz, *Ber.* **35**, 3525 (1902). (277) Biltz, Küppers, *Ber.* **37**, 2398–2423 (1904). (278) Senderens, *Compt. rend.* **146**, 1213 (1908); *Bull. soc. chim.* (4) **3**, 828 (1908). (279) Reilly (to Dow Chem. Co.), U.S. 2,140,548, 2,140,549, Dec. 20, 1938; *Cent.* **1939**, I 3625; *C.A.* **33**, 2540 (1939). (280) Reilly (to Dow Chem. Co.), U.S. 1,947,491, Feb. 20, 1934; *Cent.* **1935**, I 3345; *C.A.* **28**, 2371 (1934).

(281) Compagnie des Prod. Chim. d'Alais, etc., French 804,491, Oct. 24, 1936; *Cent.* **1937**, I 1545; *C.A.* **31**, 3509 (1937). (282) Coleman, Moore (to Dow Chem. Co.), U.S. 2,174,737, Oct. 3, 1939; *C.A.* **34**, 779 (1940). (283) Maier, Ger. 522,959, April 20, 1931; [*Cent.* **1931**, I 3607]; *C.A.* **25**, 3670: French 655,930, April 25, 1929; *Cent.* **1929**, II 1347; *C.A.* **23**, 3931 (1929). (284) Jung, Zimmermann (to I. G.), Ger. 545,993, March 8, 1932; *Cent.* **1932**, I 2893; *C.A.* **26**, 3520 (1932). (285) Hamai, *Bull. Chem. Soc. Japan* **9**, 542–548 (1934). (286) Kharasch, Brown, *J. Am. Chem. Soc.* **61**, 2145 (1939). (287) Levine (to du Pont Co.), Can. 395,846, April 15, 1941; *C.A.* **35**, 4782 (1941): Brit. 505,196, June 1, 1939; *Cent.* **1939**, II 2712; *C.A.* **33**, 7814 (1939). (288) Rodebush (to U.S. Ind. Alc. Co.), U.S. 1,402,318, Jan. 3, 1922; *Cent.* **1923**, II 960; [*C.A.* **16**, 935 (1922)]. (289) Tzyurikh, *Trans. State Inst. Applied Chem.* (*U.S.S.R.*) **24**, 70–80 (1935);

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(297) Petrenko-Kritschenko, Opotzky, *Ber.* **59**, 2131–2140 (1926). (298) Tronov, Laduigina,

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(321) Golev, *Sbornik Dikhloretan* **1939**, 11–13; *C.A.* **36**, 2042 (1942). (322) Isskra, *J. Chem. Ind. (Moscow)* **12**, 947–953 (1935); *Cent.* **1936**, I 2823; not in *C.A.* (323) S S. Drozdov, N.S.

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(331) Slator, *J. Chem. Soc.* **85**, 1297 ...
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Jan. 9, 1933; *Cent.* **1933**, II 132; *C.A.* **27**, 2159 (1933). (344) Krauss, *J. Am. Chem. Soc.* **39**, 1512–1513 (1917). (345) Stähler, *Ber.* **47**, 911–912 (1914). (346) von Braun, Dengel, Arnold, *Ber.* **70**, 992 (1937). (347) Klebanskii, Mironenko, *J. Applied Chem. (U.S.S.R.)* **14**, 618–631 (1941); *C.A.* **36**, 3500 (1942). (348) Sisido, Kato, *J. Soc. Chem. Ind. Japan* **43**, Suppl. bindg. 232–233 (1940); **44**, 25–27 (1941); *Cent.* **1942**, I 2199, 2200; *C.A.* **35**, 1026, 4369 (1941). (349) Clark, Kutz (to General Electric Co), U.S. 2,033,612, March 10, 1936; *Cent.* **1936**, II 1036, *C.A.* **30**, 2991 (1936). (350) B.A.S.F., Ger. 326,729, Sept. 29, 1920; *Cent.* **1921**, II 61; not in *C.A.*

(351) Homer, *J. Chem. Soc.* **97**, 1144–1145 (1910); Bodroux, *Bull. soc. chim.* (3) **25**, 491–497 (1901). (352) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,079,279, May 4, 1937; *Cent.* **1937**, II 1267; *C.A.* **31**, 4416 (1937). (353) Cope, *J. Am. Chem. Soc.* **57**, 574 (1935). (354) Wohl, Berthold, *Ber.* **43**, 2179 (1910). (355) Clemo, Perkin, *J. Chem. Soc.* **121**, 644–646 (1922). (356) Ernst, Berndt (to I.G.), Ger. 525,188, May 20, 1931; *Cent.* **1931**, II 1055; *C.A.* **25**, 4284 (1931). (357) Coleman, Stratton (to Dow Chem. Co.), U.S. 2,130,990, Sept. 20, 1938; *Cent* **1939**, I 2295; *C.A.* **32**, 9098 (1938) (358) Dreyfus, Brit. 166,767, Aug. 18, 1921; *Cent.* **1921**, IV 1140; *C.A.* **16**, 830 (1922). (359) I.G., French 805,563, Nov. 24, 1936; *Cent.* **1937**, I 2258; [*C.A.* **31**, 4345 (1937)]. (360) Wheeler (to Imperial Chem. Ind., Ltd.), Brit. 333,989, Sept. 18, 1930; *Cent.* **1930**, II 3638; *C.A.* **25**, 709 (1931).

(361) Meyer, Ger. 332,677, Feb. 7, 1921; *Cent.* **1921**, II 646; not in *C.A.* (362) Rodebush (to U.S. Industrial Alc. Co.), U.S. 1,430,324, Sept. 26, 1922; *Cent.* **1924**, II 1511; *C.A.* **16**, 3903 (1922). (363) Coleman, Moore (to Dow Chem. Co.), U.S. 2,021,852, Nov. 19, 1935; *Cent.* **1936**, I 1505; *C.A.* **30**, 485 (1936). (364) Engelhardt (to Bayer and Co.), Ger. 404,999, Oct. 25, 1924; *Cent.* **1925**, I 1530; not in *C.A.* (365) I.G., French 669,739, Nov. 20, 1929; *Cent.* **1930**, I 3237; [*C.A.* **24**, 1866 (1930)]. (366) N. V. de Bataafsche Petroleum Maatschappij, Brit. 496,290, Dec. 29, 1938, *Cent.* **1939**, I 2294; *C.A.* **33**, 2912 (1939). (367) Calingaert, Soroos, Hnizda, Shapiro, *J. Am. Chem. Soc.* **62**, 1545–1547 (1940): Calingaert, Beatty, Neal, *J. Am. Chem. Soc.* **61**, 2756 (1939). (368) Dougherty, *J. Am. Chem. Soc.* **51**, 579–580 (1929). (369) Kharasch, Hannum, *J. Am. Chem. Soc.* **56**, 714 (1934). (370) Lean, Lees, *J. Chem. Soc.* **71**, 1062–1068 (1897).

(371) Perkin, *J. Chem. Soc.* **65**, 578–589 (1893). (372) Bennett, *J. Chem. Soc.* **115**, 577 (1919). (373) Schouten, *Rec. trav. chim.* **56**, 542–543 (1937). (374) Schouten, *Rec. trav. chim.* **56**, 870–871 (1937). (375) Bodroux, *Compt. rend.* **208**, 1023 (1939). (376) Fränkel, Nussbaum, *Biochem. Z.* **182**, 424–433 (1927); *Cent.* **1927**, II 1340, not in *C.A.* (377) Davies, Evans, Hulbert, *J. Chem. Soc.* **1939**, 416. (378) Tronov, *J. Russ. Phys.-Chem. Soc.* **58**, 1278–1301 (1926); *Cent.* **1927**, II 1145. (379) Weber, *Chem. Ztg.* **57**, 836 (1933); *Cent.* **1933**, II 3889; *C.A.* **28**, 727 (1934). (380) Doughty, *J. Am. Chem. Soc.* **41**, 1130–1131 (1919).

(381) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144, Oct. 30, 1934; *Cent.* **1935**, I 3051; [*C.A.* **29**, 177 (1935)]. (382) Levy, Campbell, *J. Chem. Soc.* **1939**, 1443. (383) Wanag, *Ber.* **75**, 725 (1942).
2226 (1887). (386)
Wenker, *J. Am. Ch*
(390) Heppel, Neal,
(391) Lehman, S
not in *Cent.* (392)

3:5140 3,3-DICHLOROPROPENE-1 $C_3H_4Cl_2$ Beil. I - 199

(1,1-Dichloropropene-2; allylidene (di)chloride; " acrolein dichloride ")

$$CH_2{=}CH{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}H$$

Beil. I - 199, I_1—, I_2—

B.P. 84.4° cor. (1)	$D_{24.5}^{24.5} = 1.170$ (1)	
85° (5)	$D_{-}^{21} = 1.169$ (2)	$n_D^{21} = 1.450$ (2)

[*See also* 1,3-*dichloropropene*-1 (3:5280).]

Note that C̄ represents the synionic mesomer of 1,3-dichloropropene-1 (3:5280); reactions of either mesomer may under certain conditions lead to derivatives of the other; however, in practice the tendency appears to be strongly in the direction of 1,3-dichloropropene-1 (3:5280) so that most of the known reactions of C̄ yield the same products as does the mesomer; the rate of reaction, however, is generally very much slower with C̄.

[For prepn. of C̄ from acrolein (1:0115) with PCl_5 (16% yield C̄ accompanied by 32% 1,3-dichloropropene-1 and some 1,1,3-trichloropropane (3:5660) (3)) (1) (4), or from 1,1,3-trichloropropane (3:5660) with alc. KOH (5) (other products are also formed), see indic. refs.]

[C̄ with Cl_2 adds 1 mole halogen giving (4) 1,1,2,3-tetrachloropropane (3:6035), b.p. 179–180° at 756.6 mm. (4).]

[Č with conc. HCl in s.t. at 100° for 10 hrs. (4) isomerizes to 1,3-dichloropropene-1 (3:5280).]

[Č with NaOEt reacts much more slowly than its mesomer; however, after 15 hrs. refluxing with large excess NaOEt, Č gives 1-chloro-3-ethoxypropene [Beil. I-439], b.p. 126–127°, $D_{-}^{16} = 1.018$, $n_{-}^{16} = 1.438$ (3), i e, the same product as from the mesomer.]

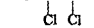
[Č with Na phenolate in abs. alc. refluxed for 4 hrs. gives (3) ω-chloroallyl phenyl ether, the same prod. as correspondingly obtd. in ½ hr. from the mesomer, q.v.]

[Č with Et_2NH in dry ether for 20 days gives (3) only a slight ppt. of diethylamine hydrochloride and but very small yield of *N,N*-diethyl-γ-chloroallylamine (cf. the mesomer).

[Č with NaOAc (3), $CaBr_2$ (3), CaI_2 (3) cf. (6), or C_6H_5MgBr (3) gives more slowly and in poor yields the same products as are formed readily from the mesomeric 1,3-dichloropropene-1 (3:5280), q.v]

3:5140 (1) Hübner, Geuther, *Ann.* **114**, 36–43 (1860). (2) Kirrmann, Grard, *Compt. rend.* **190**, 876–878 (1930), *Cent* **1930**, II 29; *C.A* **24**, 3750 (1930), *Bull soc. chim.* (4) **47**, 834–847 (1930). (3) Kirrmann, Pacaud, Dosque, *Bull soc chim.* (5) **1**, 860–871 (1934). (4) van Romburgh, *Bull soc. chim.* (2) **36**, 549–557 (1881). (5) van Romburgh, *Bull. soc. chim.* (2) **37**, 98–103 (1882) (6) van Romburgh, *Rec. trav. chim.* **1**, 234–237 (1882).

3:5150 1,2-DICHLOROPROPENE-1 (high-boilg. stereoisomer)



$C_3H_4Cl_2$ Beil. I - 199
I_1—
I_2—

B.P. 84–86° (1)

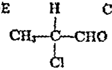
[*See also the lower-boilg. stereoisomer* (3:5110)]

[For prepn of Č from α,β,β-trichloro-*n*-butyric acid (3·0925) by soln. in aq. Na_2CO_3 and subsequent decompn. to Č (65% yield) by protracted boilg see (1).]

Č with Cl_2 adds 1 mole halogen giving (1) 1,1,2,2-tetrachloropropane (3:5825), b.p. 153–154° (1)

3:5150 (1) Szenic, Taggesell, *Ber* **28**, 2667–2668 (1895).

3:5160 α-CHLOROPROPIONALDEHYDE



C_3H_5OCl Beil. I - 632
I_1-(334)
I_2—

B.P. 86° (1) D_4^{15} = **1.182 (1)** n_D^{17} = **1.431 (1)**

Oil, spar. sol. aq.; misc. with ether, AcOH, or C_6H_6 — Č with aq. yields a hydrate, b.p 80 5–81° (2).

Č polymerizes in air to a white solid which upon htg. at 170–200° *regenerates Č* (2).

[For prepn. from *n*-propyl alc. (1:6150) by actn. of Cl_2 at 45–50° in presence of catalysts such as $AlCl_3$, CrO_2Cl_2, or Mg turnings see (3); for formn. (together with other products) from propylene oxide (1·6115) + S_2Cl_2 see (4); for other modes of formn. see Beil. I-632 and I_1-(334).]

Č on oxidn with excess alk. $KMnO_4$ yields acetic acid ac. (1:1010) (1) (2). — Č reduces $NH_4OH/AgNO_3$ in the cold and Fehling's soln. on htg. — Č gives positive fuchsin ald. test and yields a $NaHSO_3$ cpd. (1).

3:5160 (1) Brochet, *Ann chim.* (7) **10**, 311–344 (1897). (2) Oddo, Cusmano, *Gazz chim. ital.* **41**, II 232–234 (1911) (3) Bowman, *Proc S. Dakota Acad. Sci.* **19**, 112–114 (1939); *C.A.* **34**, 2786 (1940). (4) Malinovski, *J. Gen. Chem (U.S.S.R.)* **9**, 632–639 (1939); *C.A.* **34**, 375 (1940).

3:5170 1,1,2-TRICHLOROETHYLENE $HC{=}C(Cl){-}Cl$ with Cl on first carbon; C_2HCl_3 Beil. I - 187; I_1-(78); I_2-(159)

B.P.		F.P.		D		n_D	
87.55° at 765 mm.	(1)	[−73°	(14)]	D_4^{25} = 1.4597	(9)	n_D^{25} = 1.4750	(18)
88° at 760 mm.	(2)	−83°	(12)	1.4542	(5)	1.47488	(10)
87.0–87.3° at 753 mm.	(3)	−86.4°	(15)	1.4540	(17)	1.47458	(19)
87.0–87.2° at 760 mm.	(4)	−86.9°	(16)	1.454	(10)	1.4744	(8)
87.15° at 760 mm.	(5)	−88°	(9)			1.4742	(8)
86.95° at 760 mm.	(6)						
	(7) (15)			D_4^{20} = 1.477	(2)	n_D^{20} = 1.[illegible]	(20)
86.9°	(8)			1.4679	(9)		
86.7° at 760 mm.	(9)			1.4655	(4)		
86.60° at 758 mm.	(10)			1.4649	(12)		
86.0–87.5° at 760 mm.	(11)						
85.8–86.0° at 741.6 mm.	(12)						
85.9–86.0°	(32)						
83° at 680 mm.	(13)						
77.0° at 562 mm.	(5)						
65.0° at 385 mm.	(5)						
51.0° at 234 mm.	(5)						
45.0° at 183 mm.	(5)			D_4^{15} = 1.4762			
44.15° at 177 mm.	(5)			1.4695			
38.20° at 139 mm.	(5)						
30.0° at 92 mm.	(5)						
25.0° at 73 mm.	(5)						

...oos, Hu... / ...h. Chem. Soc. / ...69) Kharasch, / ...71, 1062–1068 / ...oc. 115, 577 (1919). / ...trav. chim. 56, 870– / ...ikel, Nussbaum, Bio- / ...Davies, Evans, Hulbert, / ..., 1278–1301 (1926); Cent / ...3889; C.A. 28, 727 (1934). / Oct. 30, 1934; Cent. 1935, / 1939, 1443. (383) Wanag, / ...). (385) Gabriel, Ber. 20, / ... 24, 2626 (1891). (388) / J. Chem. Soc. 1928, 728. / ...ricol. 27, 15–21 (1945). / ...30); C.A. 31, 477 (1937) / ... (1939).

Note 2. For D_4^T over range ...

Beil. I - 199; I_1—; I_2—

Note 1. For vap. press. over range 0°–86.7° see (9).

Colorless mobile liquid with sweetish odor suggesting chloroform. ... inflammable (see below).

MISCELLANEOUS PHYSICAL PROPERTIES

Various solubility relationships. $\bar{C}$ is pract. insol. aq. and eas. volatile with ... (2) soly. of $\bar{C}$ in aq. at 16° = *0.081 wt. % (23), at 18° = 0.025* wt. % (23), *0.18 m*... ml. aq. (24). — Soly. of aq. in $\bar{C}$ at −30° = 0.0025 wt. %, at −20° = 0.0050 wt. ... −8° = 0.0075 wt. %, at 0° = 0.0100 wt. %, at 6° = 0.0125 wt. %, at 10° = 0.0170 wt. %, at 20° = 0.0250 wt. %, at 25° = 0.0325 wt. % (9).

[For data on soly. in $\bar{C}$ of 248 org. cpds. see (25); for solv. actn. of $\bar{C}$ on various dyes *(in connection with use of $\bar{C}$ as dry cleaning fluid) see (26) (see also below under uses of $\bar{C}$).*]

[For soly. of I_2 in $\bar{C}$ over range 11–25° see (27); for use of such solns. in detn. of I_2 No. of oils and fats see (28). — For distrib. of I_2 between $\bar{C}$ and aq. at 25° see (30) cf. (31).]

[For soly. in $\bar{C}$ at 20° of HCl or H_2S at 1 atm. see (32).]

[For absorption of vapors of $\bar{C}$ by kerosene see (33).]

Effect of $\bar{C}$ on explosive range of various gases. *Air satd. with $\bar{C}$ at 14° conts. 5.7* vol. (?) % $\bar{C}$ (34).

[Vapor of $\bar{C}$ does not form inflammable mixts. with air at ord. temp. and press.; below

25.5° $\bar{C}$ has insufficient vap. press. to produce inflam. mixts. at total press. of 1 atm. or above even in mixts. contg. high concns. of O_2. — At high temps. vapor of $\bar{C}$ is inflammable in air, igniting at 463°; in oxygen at 419° (18). — Limits of inflammability of mixts. of $\bar{C}$ with O_2 are 10.30–64.5 vol. % $\bar{C}$ (35); for study of limits of inflam. of system $\bar{C}/O_2/N_2$ see (18) (35).]

[For study of influence of vapors of $\bar{C}$ upon explosive regions of mixts. of air with hydrogen (36) (37), with acetylene (36), with methane (38) (39) (36) (40) (41) (42), or with carbon monoxide (34) (36) (43) see indic. refs.]

Adsorption of $\bar{C}$ by various materials. [For study of adsorption of $\bar{C}$ on charcoal at 20° (44) and use in detn. of $\bar{C}$ (45) see indic. refs.; on MnO_2 see (46); on dehydrated $Al(OH)_3$ gel at 10–40° and desorption at 90–150° as means of recovery of $\bar{C}$ see (47).]

Other physical properties. [For study of evapn. rate of $\bar{C}$ see (48); for study of thermal conductivity of $\bar{C}$ see (11).]

(1) Hu...ems contg. $\bar{C}$ (see also below under azeotropes). $\bar{C}$ + *MeOH (1:6120)*: 876–878 (1930). (3) Kurmann, 1 ... p./vapor-liq. compn., D/compn., and n/compn. see (49). — $\bar{C}$ + *EtOH* *Bull. soc. chim.* ...iag. of b.p./vap.-liq. compn., D/compn., and n/compn. see (49). — $\bar{C}$ (1882). (6) van h...): for data on D_4^{25}/compn. and n_D^{25}/compn. see (10).

...study of distrib. of nicotine between $\bar{C}$ and aq. at 17° see (23).

3:5150 1,2-DICHL... . for f.p./compn. diag., eutectic, f.p. −100.2°, contg. 68.6 wt. % (high-boilg. ste... *...hloroethane (3:5880)*: for D_4^{25}/compn. data see (17) cf. (50).

B.P. 84–86° (1) ... $\bar{C}$ (see also below under azeotropes). $\bar{C}$ + *MeOH (1:6120)* ...ompn. and n/compn. diags. see (49b). — $\bar{C}$ + *EtOH (1:6130)* ...iagram in wt. % at 25° and n_D^{25}/compn. diagram in wt. % see

[*See also the lower-boilg. ste...*

...g. $\bar{C}$. *Binary azeotropes.* $\bar{C}$ + H_2O: gives a two-phase const.-

[For prepn. of $\bar{C}$ from α,β,β... pe), b.p. 73°, contg. 65 mole % $\bar{C}$ (8).

subsequent decompn. to $\bar{C}$ ... forms a const.-boilg. mixt., b.p. 60.2° at 760 mm., D_4^0 = 1.1643

$\bar{C}$ with Cl_2 adds 1 mole (52a) = 30 mole % $\bar{C}$ (52a) = 51 vol. % $\bar{C}$ (53). — $\bar{C}$ + *EtOH*

153–154° (1). ...-boilg. mixt., b.p. 70.9° at 760 mm., D_4^0 = 1.212, contg. 73 wt. %

3:5150 (1) Szenic, Tagges... $\bar{C}$ (52b) cf. (53) (54). — $\bar{C}$ + *n-propyl alc. (1:6150)*: forms a const.- ...5° at 760 mm., D_4^0 = 1.3283, contg. 83 wt. % $\bar{C}$ = 69 mole % $\bar{C}$

3:5160 α-CHLOR... *...yl alc. (1:6135)*: forms a const.-boilg. mixt., b.p. 75.5° (7), abt. 74° D_4^0 = 1.22, contg. abt. 72 wt. % $\bar{C}$ (70 wt. % $\bar{C}$ (7)) = 54 mole % $\bar{C}$ *...butyl alc. (1:6180)*: gives a const.-boilg. mixt., b.p. 86.85° at 760 mm., wt. % $\bar{C}$ (55) — $\bar{C}$ + *isobutyl alc. (1:6165)*: forms const.-boilg. mixt., b.p. 760 mm., D_4^0 = 1.396, contg. 91 wt. % $\bar{C}$ = 86 mole % $\bar{C}$ (52e). — $\bar{C}$ + *ter-butyl*

B.P. *...6140)*: forms const.-boilg. mixt., b.p. 75.8° (6), 75° (52f) at 760 mm., D_4^0 = 1.326 Oil, ...contg. 67 wt. % $\bar{C}$ (6) (84 wt. % $\bar{C}$ (52f) = 74 mole % $\bar{C}$ (52f)). — $\bar{C}$ + *ter-amyl alc.* *...60)*: forms const.-boilg. mixt., b.p. 84.5° (6), 84° (52g), D_4^0 = 1.372 (52g), contg. 80 wt. % $\bar{C}$ (6) (88 wt. % $\bar{C}$ = 83 mole % $\bar{C}$ (52g)). — $\bar{C}$ + *allyl alc. (1:6145)*: forms const.-boilg. mixt., b.p. 80.95° at 760 mm., D_4^0 = 1.335, contg. 84 wt. % $\bar{C}$ = 70 mole % $\bar{C}$ (52h).

$\bar{C}$ + *AcOH (1010)*: forms const.-boilg. mixt., b.p. 86.5° at 760 mm., contg. 96.2 wt. % $\bar{C}$ (6).

$\bar{C}$ + *1,2-dichloroethane (ethylene dichloride) (3:5130)*: forms a const.-boilg. mixt., b.p. 82.9° at 760 mm., contg. abt. 18 wt. % $\bar{C}$ (6).

Ternary azeotropes. $\bar{C}$ + *EtOH (1:6130)* + H_2O: forms a ternary heteroazeotrope, b.p. 67.25° at 760 mm., contg. 38.4 mole % $\bar{C}$ + 41.2 mole % EtOH + 20.4 mole % H_2O (56a): note that this azeotrope conts. 69.4 vol. % $\bar{C}$ + 23.8 vol. % EtOH + 6.8 vol. % H_2O (53), and that upon condensation at 15° it separates into two layers, the upper having the composition 0.8 vol. % $\bar{C}$ + 7.2 vol. % EtOH + 5 vol. % H_2O (total upper layer = 13

vol. %), the lower having the composition 68.6 vol. % C̄ + 16.6 vol. % EtOH + 1.8 vol. % H_2O (total lower layer = 87%) (53). — For further discussion and data see also (8) (49).

C̄ + n-propyl alc. (1:6150) + H_2O: forms a ternary heteroazeotrope, b.p. 71.55° at 760 mm., contg. 51.1 mole % C̄ + 16.6 mole % *n*-propyl alc. + 32.3 mole % H_2O (56b).

C̄ + allyl alc. (1:6145) + H_2O: forms a ternary heteroazeotrope, b.p. 71.4° at 760 mm., contg 49.2 mole % C̄ + 17.3 mole % allyl alc. + 33.5 mole % H_2O (56c).

USES OF C̄

Most of the utility of C̄ in industry depends upon its physical properties especially as a solvent; these applications include the dehydration of alcohols and acids, degreasing of metal, wool, and leather, dry cleaning of fabrics, extracting of oils from seeds, etc.; dewaxing of mineral lubricating oils, use as fumigant and insecticide, refrigerant, etc. [For an excellent brief survey of these uses see (57) (58); for further and more recent examples see below.]

Use in dehydration of alcohols. [For use of C̄ in dehydration of EtOH (or MeOH) by azeotropic distn. (Drawinol process) see (8) (49) (53) (59) (60) (61) (62); for patents on this method see (63). — For use of C̄ in denaturing alc. see (64).]

Use in dehydration of acids. [For use of C̄ in concn. of AcOH (1:1010) see patents (65) (66). — For sepn. of AcOH (1:1010) from formic acid (1:1005) by distn. of mixt. with C̄, the condensate sepg. into an upper layer of an azeotropic mixt. of C̄ + formic acid, the lower layer being C̄ see (67).]

Use of C̄ for degreasing of metal. [For patents on use as metal degreaser of mixts. of C̄ + an alc. + soap (68), C̄ + oleic acid (69), C̄ + ethylene dichloride (3:5130) (70) (71), or C̄ (72) (73) see indic. refs. — *For use of C̄ + rosin + boiled linseed oil in cleaning and* leaving coating preparatory to etching see (74). — Because of great toxicity of C̄ (see below) special attention (75) must be given to ventilation of degreasers using it.]

Use of C̄ in dry cleaning of fabrics. Because of its solvent power supported by its low b.p. and non-inflammability C̄ is widely used as dry cleaner's solvent [for general articles from this viewpoint see (76) (77) (78); for patent see (79); for solv. actn. of C̄ on dyes see (26)].

Use of C̄ in extraction of fats and oils. [For use of C̄ as solv. for extraction see (81) (82) (83). — For use of C̄ for extraction of soybean oil (84) including n_D^{25} and D in g/cc. at 77°, 100°, and 122° F. (19) see indic. refs. — For study of losses of C̄ in extn. of fats see (85).]

[For use of C̄ in detn. of fats in foods (butter, margarine, etc.) see (86) (87).]

[For use of C̄ in detn. of aq. in fats and oils see (88); cf. use of acetylene tetrachloride (3:5750) for this purpose]

Use of C̄ in dewaxing of mineral lubricating oils. [For articles including use of C̄ for this purpose see (89) (90); for patents see (91).]

Use of C̄ as fumigant, insecticide, etc. [For comparative tests of C̄ see (92); for patents on such use of C̄ (93) or mixts. contg. C̄ (94) see indic. refs.]

Use of C̄ as component of refrigerating liquids. [For use of C̄ with dichloroethylene (3:5030) see (95) cf. (96); for use of C̄ or its mixts. in low-temp. cryostats see (16).]

Miscellaneous uses of C̄. [For use of C̄ with MeBr (97) or with CCl_4 (98) as fire extinguishing compn. see indic. refs.; for use of C̄ as boiler or radiator cleaner (99) or as rust-retarder (100) see indic. refs.; for use of C̄ as weed-killer see (101); for addition to liq. HCN to diminish inflammability see (102); in prepn. of starch see (103); in recrystn. of T.N.T. see (104); for use as solv. in ebullioscopy ($K = 44.3$ per 100 g. solv.) see (105); to replace xylene in histological technique see (106) (107) (108).]

PHYSIOLOGICAL BEHAVIOR OF $\bar{C}$

$\bar{C}$ is one of the more toxic of the group of chlorinated solvents; it is absorbable into the body not only by inhalation but also through the skin (109). — Although full detailed treatment of this aspect of $\bar{C}$ is beyond the scope of this work, yet the following citations will be found useful as lead references for further information.

Toxicity of $\bar{C}$. [For important surveys of physiological properties (110), toxicity (111), comparative toxicity of $\bar{C}$ and CCl_4 (112) see indic. refs.]

[For studies of liver injury by $\bar{C}$ (113), of anemia from $\bar{C}$ (114), of American cases since 1932 of industrial poisoning by $\bar{C}$ (115), or role of impurities in toxicity of $\bar{C}$ (116), of industrial hazards of $\bar{C}$ (117) (118) (119), of relation between toxicity and b.p. (120) see indic. refs. — For other studies of toxicity or of poisoning by $\bar{C}$ see (121)–(130), incl.]

$\bar{C}$ as narcotic, anesthetic, analgesic, etc. [$\bar{C}$ has very important use in treatment of trigeminal neuralgia (131) (132) (133); for toxic effects of $\bar{C}$ after long use as antineuralgic see (134), for chem. exam. of $\bar{C}$ for medical use see (21).]

[For use of $\bar{C}$ as anesthetic see (135) (136) (137); for use of $\bar{C}$ in treatment of migraine see (138); for effect on pain threshold see (139); for neural depressing effect (140) and narcotic actn. of $\bar{C}$ (141) (142) (143) (144) see indic. refs.]

[For studies of antiseptic and disinfectant actn. of $\bar{C}$ see (145) (146) (147) (148) (149) (150) (24)]

Miscellaneous related topics. [From dogs after inhalation anesthesia with $\bar{C}$ from 5–8% of initial $\bar{C}$ is excreted (151) as trichloroacetic acid (3:1150). — For study of anthelmintic actn. of $\bar{C}$ see (152). — For actn. of $\bar{C}$ on alc. fermentation see (153).]

DETERMINATION OF $\bar{C}$

By physical methods. For detn. of $\bar{C}$ (as vapor) by use of the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer (154)) see (155); this instrument will measure $\bar{C}$ in concns. of 10–2000 p.p.m. and is insensitive to methyl chloride (3:7005), methylene (di)chloride (3:5020), $CHCl_3$ (3:5050), CCl_4 (3:5100), vinyl chloride (3:7010), ethylene (di)chloride (3:5130), acetylene tetrachloride (3:5750), and to many (but not all) common non-chlorinated solvents such as methyl, ethyl, and amyl alcohols, ethyl acetate, etc.; for details see (155). — For detn. of $\bar{C}$ in air by adsorption on charcoal see (45).

By chemical methods. *Those involving decomposition of $\bar{C}$ and subsequent detn. of resultant chloride ion.* One class of these methods involves pyrolytic decomposition of $\bar{C}$ by appropriate htg. (156) (157) cf. (158) (159) cf. (127); note that $\bar{C}$ with air at 900–1000° gives exclusively $CO_2 + HCl$, provided that concn. of $\bar{C}$ is not more than 12 mg. per liter; above this amt. from 2–20% of the total carbon and chlorine are converted to $CO + Cl_2$, but $COCl_2$ (3:5000) is *not* found up to concns. of 100 mg. $\bar{C}$ per liter (159). — For variation of the pyrolytic method involving burning of $\bar{C}$ (or solns. of $\bar{C}$) in a lamp see (160) (161) (162) (163) (164).

A second class involves decomposition of $\bar{C}$ by chem. means, e.g., by use of Na + ethanolamine in dioxane (165) (166), or by complete hydrolysis of $\bar{C}$ with excess aq. 25% KOH in s.t. at 150° for 1 hr. (167).

Note that $\bar{C}$ on oxidn. with CrO_3/H_2SO_4 as directed (168) gives quant. CO_2.

Detn. of $\bar{C}$ by conversion to mercuric trichloroethylenide $Hg(CCl=CCl_2)_2$. $\bar{C}$ with aq. KOH soln. of $Hg(CN)_2$ on shaking 24 hrs at room temp. ppts. (169) $Hg(CCl{=}CCl_2)_2$ (for amplification see below under *behavior of $\bar{C}$ with inorganic reacts.*). — For use of this method in detn. of $\bar{C}$ even in pres. of methylene (di)chloride (3:5020), $CHCl_3$ (3:5050), CCl_4 (3:5100), 1,2-dichloroethylene (3:5030), or tetrachloroethylene (3:5460) see (169).

Detn. of C̄ colorimetrically by use of Fujiwara reaction with pyridine + alkali. C̄ with pyridine + aq. alk. gives on short warming a red coloration (similar to but recognizably different from the red-violet color obtd. with $CHCl_3$) which on further warming changes to orange; for use of this color in detn. of C̄ in air (accuracy ±11% except that at concns. of C̄ as low as 20 p.p.m. error may be as much as 50%) see (170) cf. (111) (127); for use in detn. of C̄ in animal tissue see (171); for table of sensitivity of this test under comparable conditions from C̄ as compared with $CHCl_3$ (3:5050), CCl_4 (3:5100), 1,1,2-trichloroethane (3:5320), 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750), and tetrachloroethylene (3:5460) see (151).

PREPARATION OF C̄

The principal method of preparation or manufacture of C̄ is from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by elimination of 1 HCl (see below), but it is formed as a by-product from various other reactions (see below). — [For general reviews of prepn. of C̄ and its relationships with other "chlorinated solvents" see (31) (172).]

From 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750). *By pyrolytic loss of HCl (dehydrochlorination).* [For prepn. of C̄ from acetylene tetrachloride in s.t. at 300° for 15 hrs. (173), over pumice at 700° (174) or 400–500° (175), over pumice + cat. at 500° (176), over pumice contg. $Cu_3(PO_4)_2$ at 450–500° (177), over ThO_2 below 390° (178), over $BaCl_2$ at 300° (179), over bone char at 300–310° (180), over activated carbon at 200–300° (181), 260° (182), or 500° (176) see indic. refs. — Note claim (183) that formn. of C̄ by dehydrochlorination of acetylene tetrachloride over charcoal at 250–300° is not effective and yield of C̄ diminishes with increase of temp.]

By pyrolytic loss of HCl in pres. of an org. acceptor. [For prepn. of C̄ from acetylene tetrachloride (3:5750) or pentachloroethane (3:5880) or 1,1,1,2-tetrachloroethane (3:5555) with acetylene over cat. at 250° (181) cf. (184) or with MeOH over Al_2O_3 at 280° (185) see indic. refs.]

By loss of HCl in pres. of an inorganic acceptor. [For prepn. of C̄ from acetylene tetrachloride (3:5750) by htg. with aq. alk. or alk. carbonates (186) in pres. of tetraethylene glycol, etc., as promoter (187), or with aq. $Ca(OH)_2$ or alk. carbonates (186) (188) (192) (193) (for test of Ger. 171,900 (186) see (190) (191)), or with alc. KOH (194) (195) cf. (173), or with alc. NaOEt (194) see indic. refs.]

[For prepn. of C̄ from acetylene tetrachloride (3:5750) by elimination of 1 HCl with excess NH_3 gas in pres. of aq. at 60–70° (196), with conc. aq. NH_4OH at 160–170° (196) (191) (for test of Ger. 351,463 (196) see (191)), with liq. NH_3 at −40° (13) (197), or by refluxing with dry pyridine (198), or by action of C_6H_5MgBr (199) see indic. refs.]

Note on impurities in C̄. Note that tech. C̄ obtained from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) by elimination of HCl often contains in its high-boilg. fractions ("Tri-Nachlauf" and "Tetra-Nachlauf") other chlorinated materials such as 1,1,2,3,4,4-hexachlorobutane (3:3155), 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), solid 1,2,3,4-tetrachlorobutadiene-1,3 (3:0870), liq 1,2,3,4-tetrachlorobutadiene-1,3 (3:6150), and hexachloroethane (3:4835), (207). — [For use of these "Nachlaufe" as insecticides and weed-killers see (268).]

From other halogenated ethanes. [For formn. of C̄ from 1,2-dichloroethane (ethylene dichloride) (3:5130) as by-product (29% yield) of action of Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 400–480° (200), or as by-product of actn. of Cl_2 in u.v. light (201), see indic. refs.]

[For formn. of C̄ from 1-bromo-1,1,2-trichloroethane by elimination of HBr with hot alc. Na phenolate (60% yield) see (245).]

[For formn. of C̄ from pentachloroethane (3:5880) with acetylene over cat. at 250° (181), or with H_2 over Ni at 270° (22) (note that C̄ resists further hydrogenation; also

that pentachloroethane over $NiCl_2$ without H_2 yields (22) tetrachloroethylene (3:5460)), or by actn. of MeMgI (203) see indic. refs. — For formn. of C̄ from 1,1,2-trichloro-1,2-dibromoethane with H_2 over NI at 300° or without H_2 over $BaCl_2$ at 400° see (202).]

From miscellaneous sources. C̄ is formed as a by-product of actn. of acetylene with Cl_2 but no citations will be given here [for formn. of C̄ from chloral (3:5210) with P_2S_5 at 160–170° (204) or from di- or tri-thioparachloral on dry distn. (205), or from 2-(trichloroacryloyl)-3-sulfamidobenzoic acid by alk. hydrolytic cleavage (206), see indic. refs.].

CHEMICAL BEHAVIOR OF C̄

Pyrolysis of C̄. [C̄ passed over pumice at 700° decomposes yielding (174) methylene (di)chloride (3.5020), $CHCl_3$ (3:5050), CCl_4 (3:5100), 1,1,1,2-tetrachloroethane (3:5555), pentachloroethane (3:5880), hexachloroethane (3:4835), 1,2-dichloroethylene (3:5030), tetrachloroethylene (3:5460), pentachlorobenzene (3:2290), hexachlorobenzene (3:4939), and other prods.]

Hydrogenation. [C̄ resists hydrogenation even with H_2 over Ni at 270° (22). — Note, however, that C̄ with HI in sunlight for 2 weeks in absence of air at room temp. is partially (25% (245)) reduced to 1,1,2-trichloroethane (3:5330).]

Oxidation. C̄ on total oxidation with CrO_3/H_2SO_4 as directed (168) gives quant. CO_2. — C̄ over chlorinated CuO at 450° gives $CO_2 + H_2O$ accompanied (209) by some phosgene (3:5000).

[C̄ with O_2 in ultra-violet light (210) (198) (211) or in pres. of cat. (e g., Br_2, I_2, H_2SO_4, HNO_3, etc.) (212) (213) (214) yields dichloroacetyl chloride (3:5290). — Note that C̄ in absence of O_2 is not decomposed either by direct or diffused sunlight (9).]

[For study of auto-oxidn. of C̄ see (215); for study of acidity developed from C̄ with air or oxygen over range −23° to 150° see (9).]

[C̄ with O_3 gives (215) a very unstable ozonide which decomposes into phosgene (3:5000), CO, HCl, and oxides of chlorine.]

Stabilization. Since in the presence of O_2 (air) C̄ has a definite tendency toward oxidation (see above), much study has been given to the problem of its stabilization by addn. of small amts of other materials. — [For general study of the stability of C̄ under a wide variety of conditions see (9); for study of method of testing stability and the efficacy of various stabilizers see (216), for use of 2–3% of EtOH (1:6130) or of cyclohexane (1:8405) as stabilizers see (217).]

For stabilization of C̄ a wide variety of compds. have been recommended in the patent literature [e.g., for use of 0.01% or less of hydroquinone monomethyl ether (1:1435) or hydroquinone monobenzyl ether (1:1539) see (218); for use of 0.1% or less of *p-ter*-butylphenol (1:1510) or *p-ter*-amylphenol (1:1495) see (219); for use of 0 001% *n*-hexylresorcinol (1:1465) see (220); for use of oil-sol. azo dyes contg. phenolic groups see (221); for use of various phenols, amines, and aminophenols see (222) (235); for use of very small amts. alc. NH_3 see (223); for use of trimethylamine (228) di-isopropylamine (224), triethylamine (225) (226), or other alkylamines (226), various nitrogenous cpds. such as dialkylated cyanamides, allylthiourea, hexamethylenetetramine, propionitrile, etc. (227), pyridine (228), caffeine (229), see indic. refs.].

[For stabilization of C̄ with mercaptans, e.g , *n*-butyl mercaptan (230), with amylene (231) cf. (222), with gasoline (232), with alk. oleate (233), with fatty acids or soaps (234) see indic. refs.]

Polymerization. C̄ under certain conditions reacts with itself forming dimeric, trimeric, and prob. polymeric products [e.g., C̄ in glass, porcelain, or enameled vessels at 180–210° under press. (236) and in pres. of small amts. of various antioxidants (237) gives a dimer, a hexachlorobutene (b.p. 200° at 710 mm.) of undetermined structure, accompanied by

higher polymers and by hexachlorobenzene (3:4939); $\bar{C}$ at elev. temp. and press. or under reflux in pres. of peroxides (such as Bz_2O_2) gives (238) (239) mainly dimer, accompanied by some trimer and polymer; $\bar{C}$ with $AlCl_3$ gives on refluxing (240) a mixt. of resinous polymers suitable (especially in mixts. with trichlorobenzene) for use as electric-insulating material].

[For copolymerization of $\bar{C}$ with various dienes (such as chloroprene (3:7080), etc.) see (241).]

Reaction with halogens. *Behavior with fluorine.* [$\bar{C}$ with F_2 at 0° for 10 hrs. gives (242) by addition 1,2-difluoro-1,2,2-trichloroethane, b.p. 72.3–72.6°, $D_4^{20} = 1.5555$, $n_D^{20} = 1.3967$, accompanied by other prods. such as 1-fluoro-1,2-dichloroethylene, and a hexachlorobutene (3:9050), m.p. 9.5–11.0°, b.p. 125.5° at 25 mm., $D_4^{20} = 1.6880$, $n_D^{20} = 1.5442$, which, however, is *not* 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), etc.]

Behavior with chlorine. $\bar{C}$ under appropriate circumstances adds 1 mole Cl_2 giving pentachloroethane (3:5880) [e.g., for study of addn. of Cl_2 at 80°, 95°, and 115° in light of 4360 Å see (243); note, however, that reaction may go further and that $\bar{C}$ with Cl_2 over activated charcoal at 60–70° either in light or in dark gives (98% yield (244)) hexachloroethane (3:4835)].

Behavior with bromine. $\bar{C}$ readily adds 1 mole Br_2 (245) (even when used as Br_2 aq. (202)) yielding 1,2-dibromo-1,1,2-trichloroethane, b.p. 204° dec. at 760 mm. (245), 125–126° at 85 mm. (202), 116.5° at 50 mm. (245), $n_D^{20} = 1.5710$ (245). [For study of rate of addn. to $\bar{C}$ of Br_2 in CCl_4 see (246).]

Behavior with iodine or thiocyanogen. $\bar{C}$ does *not* add I_2 (Wijs method) or $(SCN)_2$ (Kaufmann method) (167).

Behavior with halogen hydrides. *Reactn. of $\bar{C}$ with dry HCl.* $\bar{C}$ (1 mole) with dry HCl gas (1.57 moles) in pres. of anhydr. $FeCl_3$ (0.003 mole) in dark 6 days at room temp in abs. of air or peroxides, or $\bar{C}$ (1 mole) with dry HCl gas (1.62 moles) in pres. of $AlCl_3$ (0.004 mole) in dark 3 days at 0° in abs. of air or peroxides gives exclusively (245) (yields: 49% and 22%, respectively) 1,1,1,2-tetrachloroethane (3:5555). [Note that $\bar{C}$ with dry HCl in pres. of 5–10% $AlCl_3$ at 30–40° gives (86–88% (247)) 1,1,1,2-tetrachloroethane (3:5555), but that $\bar{C}$ + $AlCl_3$ with dry HCl at 50° gives also (248) the *sym.*-1,1,2,2-tetrachloroethane (3:5750), two pentachlorobutadienes (cf. (249)), and hexachlorobenzene (3:4939).

Reaction of $\bar{C}$ with dry HBr. $\bar{C}$ in the pres. of an anti-oxidant does *not* react with HBr even after several days at 100° or after 30 days in sunlight (245).

However, $\bar{C}$ in the pres. of suitable cat. adds HBr readily, but the mode of addn. differs according to conditions: e g., $\bar{C}$ + HBr in pres. of small amts. $FeCl_3$ or $AlCl_3$ gives exclusively in yields up to 81% (245) 1-bromo-1,1,2-trichloroethane, b.p. 152° at 760 mm., b.p. 54° at 20 mm., $n_D^{20} = 1.5217$ (245); but $\bar{C}$ with HBr in pres. of air and/or peroxides gives exclusively in yields up to 91% 2-bromo-1,1,2-trichloroethane, b.p. 171° at 760 mm., b.p. 68.9° at 20 mm., $n_D^{20} = 1.5302$, $n_D^{14.5} = 1.5326$ (245).

Behavior of $\bar{C}$ with dry HI. $\bar{C}$ does *not* add HI even after 4 days at room temp. in dark and abs. of air; on exposure of the system for 2 weeks in sunlight 25% of $\bar{C}$ was *reduced* to 1,1,2-trichloroethane (3:5330) (245).

Behavior with oxygenated mineral acids. *Reaction of $\bar{C}$ with H_2SO_4.* [$\bar{C}$ with strong H_2SO_4 at elev. temp. undergoes reactns. leading ultimately (250) (189) to high yields of chloroacetic acid (3:1370). — For patents exemplifying various conditions see (251) (252) (253) (254) (255) (256). — Note also that the H_2SO_4 may be replaced by arom. sulfonic acids such as benzenesulfonic acid, etc. (257)]

[$\bar{C}$ with fumg. H_2SO_4 (10% SO_3) shaken at 88° for ¾ hrs. gives (258) cf. (255) (259) α-chloro-α-sulfoacetic acid.]

Reaction of $\bar{C}$ *with* HNO_3. [$\bar{C}$ with conc. HNO_3 ($D = 1.42$, 4 vols.) refluxed 3 hrs. gives mainly (260) cf. (258) dichlorodinitromethane [Beil. I-78, I_1-(21), I_2-(44)], accompanied by some trichloronitromethane (chloropicrin); for behavior of $\bar{C}$ with N_2O_5 in s t. at 50° for 6 hrs. see (260).]

Behavior with alkali. $\bar{C}$ in either aq. susp. or alc. soln. does *not* neutralize $N/10$ aq. alk. (261) (for contrary earlier claim see (262)), but $\bar{C}$ with excess 2 N MeOH/KOH in s.t. at 100° for 30 min. uses alk. corresp. to 2 moles, i.e , apparent Sap. Eq. = M.W /2 = 65.8.

[$\bar{C}$ with aq. alk. or alk.-earth hydroxides at 175° under press. in pres. of copper salts is claimed (263) to yield salts of glycolic acid (1.0430).]

[$\bar{C}$ with ether passed as vapor with N_2 over solid KOH + CaO at 130° loses HCl giving (84–90% yield (264)) dichloroacetylene (3:5010) in the form of its mol cpd. (1:1) with ether, for earlier work in which $\bar{C}$ alone over solid granular KOH at 130° gives (65% yield (265)) dichloroacetylene (266) see indic. refs.]

[$\bar{C}$ with EtOH/NaOEt at 60–75° condenses with elimination of NaCl giving (yields: 81% (267), 70% (268)) (269) (204) α,β-dichlorovinyl ethyl ether (3:5540). — Note that reaction of $\bar{C}$ with alc. NaOEt has been accompanied by spontaneous explosions or ignition (270) (271) (272), presumably because of some formn of either chloroacetylene (3:7000) or dichloroacetylene (3.5010) or both cf. (273).]

[For study of stability of $\bar{C}$ toward water under various conditions see (9); note that carefully purified $\bar{C}$ is more stable toward aq. than ord. tech. product (274).]

Behavior with metals. [For study of corrosive actn of $\bar{C}$ on soft steel, copper, brass, lead, aluminum, etc , at temps. 50–150° under various conditions see (9) (275) (276) (277) (278) (279) (280) (281). — For study of sensitivity to mechanical shock of $\bar{C}$ with Li, Na, K, Ca, Sr, Ba see (282).]

Behavior with inorganic metal salts. *With* $AlCl_3$. [$\bar{C}$ with $AlCl_3$ (4–5%) on refluxing several hours (249) or $\bar{C}$ at 225–230° under press. in pres. of Fe cpds. (284) undergoes bimolecular condensation with elimination of HCl and formn. of pentachlorobutadienes; see also comments above on reaction of $\bar{C}$ with HCl and remarks below on reaction of $\bar{C}$ with other org. chlorine cpds.]

With $AlBr_3$. [$\bar{C}$ with $AlBr_3$ as directed (283) undergoes halogen interchange giving 1,1,2-tribromoethylene [Beil. I-191, I_1-(81), I_2-(164)], b p. 163–164°.]

With $FeCl_3$ [$\bar{C}$ with anhydr. $FeCl_3$ in s.t. at 85° yields (215) pentachloroethane (3:5880), but various side reactions result also in some hexachloroethane (3:4835) and tetrachloroethylene (3:5460).]

Behavior with other miscellaneous inorganic reactants. [$\bar{C}$ with excess Cl_2O in CCl_4 at −20° gives (285) pentachloroethane (3:5880), chloral (3:5210), and octachlorodiethyl ether (3:0738). — $\bar{C}$ with nitryl chloride ($ClNO_2$) in s.t. at 100° for 3 hrs. gives (286) by addn. 1,1,1,2-tetrachloro-2-nitroethane, colorless oil, b.p. 76° at 18 mm (286). — $\bar{C}$ with S_2Cl_2 in s.t. at 140–150° for some hours (no reaction in open tube) gives mainly (287) pentachloroethane (3:5880).]

[For an attempt to react $\bar{C}$ with hydrazine hydrate in pres. of solid KOH see (288).]

BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

(See also above under $\bar{C}$ with alkali.)

Behavior with hydrocarbons. [$\bar{C}$ with C_6H_6 in pres. of Al/Hg yields (289) both 1,1-diphenylethane [Beil. V-605, V_1-(285), V_2-(511)] and 1,1,2,2-tetraphenylethane [Beil. V-739, V_1-(371), V_2-(673)]. — $\bar{C}$ (1 mole) with cyclopentadiene (2 moles) at 175–185° under press. yields (309) a Diels-Alder type adduct, b p. 158–160° at 11 mm., which with phenyl azide gives (309) a hydrotriazole, m.p. 225–226°.]

Behavior with other halogenated hydrocarbons (for reaction of $\bar{C}$ with itself see above under polymerization).

With $CHCl_3$ (3:5050). [$\bar{C}$ in the pres. of $AlCl_3$ at 20° adds $CHCl_3$ to its unsatd. linkage yielding (290) (291) 1,1,1,2,3,3-hexachloropropane (3:6460); note that at higher temp., e.g., 50–60°, yield is greatly diminished and several other prods. (290) are formed.]

With CCl_4 (3:5100). [$\bar{C}$ in the pres. of $AlCl_3$ adds CCl_4 to its unsatd. linkage giving at 20–30° for 48 hrs. (49% yield (292)) (290) (291) 1,1,1,2,3,3,3-heptachloropropane (3:6860).]

With 1,1,2-trichloroethane (3:5330). [$\bar{C}$ in the pres. of $AlCl_3$ adds 1,1,2-trichloroethane to its unsatd. linkage, then loses HCl, giving after 7 days at 40° a small yield (293) of 1,1,1,4,4-pentachlorobutene-2 (3:9054) accompanied by much resin.]

With hexachloropropene (3:6370). [$\bar{C}$ (1 mole) with $AlCl_3$ + hexachloropropene (1 mole) in CH_2Cl_2 (3:5020) or $CHCl_3$ (3:5050) at 30–37° gives (82% yield (294)) 1,1,2,3,3,-4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p. 128° at 2–3 mm., 86° at 0.2 mm., $D_{20}^{20} = 1.812$, $n_D^{20} = 1.5703$ (294): $\bar{C}$ (2 moles) with $AlCl_3$ + hexachloropropene (1 mole) as directed gives in 5 hrs. at 20° a mixt. of two dodecachloroheptenes ($C_7H_2Cl_{12}$), one m.p. 94–96°, the other m.p. 58–62° (294).]

Behavior with paraformaldehyde (1:0080). [$\bar{C}$ with paraformaldehyde in the pres. of conc. H_2SO_4 at 20–25°, followed by treatment with aq., yields (295) $O{=}(CH_2.CHCl.COOH)_2$; note, however, that $\bar{C}$ with paraformaldehyde + conc. H_2SO_4 + an alkyl hydrogen sulfate (296) or an alcohol (297) (to yield the alkyl hydrogen sulfate) gives the corresp. alkyl esters of α-chloroacrylic acid (3:1445).]

Behavior with organic OH or SH cpds. [$\bar{C}$ with alc. NaOEt (see above under behavior of $\bar{C}$ with alkali) at 60–75° gives (yields: 81% (267), 70% (268)) (269) (204) α,β-dichlorovinyl ethyl ether (3:5540).]

[$\bar{C}$ (1 mole) with sodium salt of C_2H_5SH (1 mole) in abs. alc. refluxed 2 hrs. gives (298) *both* α,β-dichlorovinyl ethyl thioether, b.p. 77–80° at 30 mm., and $C_2H_5S.CH{=}C(SC_2H_5)_2$, b.p. 135–140° at 20 mm.]

[$\bar{C}$ (1 mole) with sodium salt of C_6H_5SH (either 1 mole or excess) in abs. alc. refluxed 24 hrs. gives α,β-dichlorovinyl phenyl thioether, b.p. 145–150° at 22 mm. (298).]

Behavior of $\bar{C}$ with aromatic amines. *With aniline.* $\bar{C}$ (1 mole) with aniline (3 moles) + aq. 15% NaOH (3 moles) refluxed for 40 hrs., and any unreacted components then removed by steam distn., gives (crude yield 64% (288)) N-phenylglycine-(N,N-diphenylamidine), $C_6H_5NH.CH_2.C({=}N.C_6H_5).NHC_6H_5$ [Beil. XII-557] (also known as "Sabanejev's base"), colorless cryst. from AcOEt or by rapid crystn. from hot alc., m.p. 189–190° (288). — [Note that this Sabanejev's base may be hydrolyzed in two distinct stages: e g., on protracted refluxing with EtOH (288) it splits off 1 mole aniline leaving N-phenylglycine anilide = $C_6H_5NH.CH_2.CO.NHC_6H_5$ [Beil. XII-556], cryst. from dil. alc., m.p. 112–113° (288); on the other hand the Sabanejev's base (or the N-phenylglycine anilide) on more vigorous treatment, e.g. with boiling aq. $Ca(OH)_2$, etc., hydrolyzes further yielding N-phenylglycine (N-phenylaminoacetic acid) [Beil. XII-468, XII_1-(263)], m.p. 127–128° (an important starting point for prepn. of indigo). — For patents on the prepn. of N-phenylglycine from $\bar{C}$ by reactn. with aniline in the pres. of aq. $Ca(OH)_2$ at 170–180° under press. see (299) (300).]

[The reactn. of $\bar{C}$ with aniline + aq. alk. to form Sabanejev's base (above) is also accompanied by various side reactions, including formn. (29% yield (301)) of 1,1,2-tri-(anilino)ethylene, m.p. 147° dec. (301); for further details on this and other by-products see (301) (302).]

With other aromatic amines. [For analogous behavior of $\bar{C}$ with other aromatic prim. amines in the pres. of aq. alk., e.g., with p-toluidine (288) (302) (303) (note that o-toluidine behaves abnormally while m-toluidine does *not* react (288)), β-naphthylamine (302) cf.

(288), p-anisidine (288), p-phenetidine (288), p-aminobiphenyl (288), and many others (288) see indic. refs.]

COLOR TESTS FOR Č

Ⓟ **Color test with α-naphthol (1:1500).** Č with a few drops 2% alc. α-naphthol + conc. H_2SO_4 (2 ml.), shaken, diluted with aq. (1–2 ml.), gives red-peach color (304). [This test was devised especially for detection of Č in oils or melted fats (2-ml. samples); in olive oil Č can be detected in 1/2000, and can also be noted in presence of castor oil, grapeseed oil, raw linseed oil, lard, etc. Note, however, that test fails with oils which have been subjected to oxidn., e.g., boiled linseed oil, and its sensitivity is *improved* by the pres. of reducing agts., e.g., by a trace of Zn dust (304).]

Ⓟ **Color test with cyclopentanol (1:6412).** Č (1 drop) with cyclopentanol (2 ml.) + *trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85% H_2SO_4, stood* 1 min., and shaken gives (305) green color. [Note that this same response is also *shown by* 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) but *not* by methylene dichloride (3:5020), $CHCl_3$ (3:5050), CCl_4 (3:5100), ethylene dichloride (3:5130), pentachloroethane (3:5880), *cis* (3:5042) or *trans* (3:5028)-1,2-dichloroethylene, or tetrachloroethylene (3:5460); for sensitivity for Č see (305).]

Ⓟ **Color test with pyridine and aq. alk. (Fujiwara reaction).** See above *under detn. of* Č.

Comment on behavior of Č with $NH_4OH/CuCl$. Note that Č with $NH_4OH/CuCl$ does *not* give blue color within 5 min. (306) (diff. from pentachloroethane (3:5880) q.v.

Ⓓ **Mercury** ***bis*-(trichloroethylenide), $Hg(-CCl{=}CCl_2)_2$** (see also above under detn. of Č). — Č with aq. KOH soln. of $Hg(CN)_2$ on shaking 24 hrs. at room temp. (169), or Č with HgO + NaOEt + KCN in alc. shaken 1 hr. at 40–60° (not higher) (307) (308) cf. (273), gives (yields. 100% (169), 90% (307)) mercury *bis*-(trichloroethylenide), cryst. from ether or $CHCl_3$, m.p. 83° (169) (273), 82–83° (242) (note that after recrystn. from alc. a m.p. of 141° (307) has been reported). [For behavior of ordinary 1,2-dichloroethylene with aq. alk. $Hg(CN)_2$ solns. yielding mercury *bis*-(chloroacetylide) $Hg(-C{\equiv}CCl)_2$, m.p. 185°, see text of that cpd. (3:5030).]

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Nov. 24, 1936; Cent. 1937, I 2258;
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(210)

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C.A. **22**, 4132 (1928).

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14, 285 (1920). (197) Pogosyan, Mkryan, Russ. 50,533, Feb. 28, 1937; *Cent.* **1938**, II 412;

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20, 1938;

(201) Rodebush (to U.S. Ind. Alc. Co.), U.S. 1,402,318, Jan 3, 1922; *Cent.* **1923**, II 960; [*C.A.* **16**, 935 (1922)]. (202) Mailhe, *Bull. soc. chim.* (4) **29**, 538–539 (1921). (203) Rebek, Mandrino, *Oesterr. Chem. Ztg.* **41**, 363–364 (1938); *Cent.* **1939**, I 919; *C.A.* **33**, 1266 (1939). (204) Paterno, Oglialoro, *Ber.* **7**, 81 (1874). (205) Chattaway, Kellett, *J. Chem. Soc.* **1939**, 2914. (206) Zincke, *Ann.* **416**, 69, 71, 81 (1918). (207) Müller, Hüther, *Ber.* **61**, 589–600 (1931). (208) Kaufler, Schwaebel (to A. Wacker Soc. Elektrochem. Ind.), Ger. 465,178, Sept.

(1924). (210)

; *C.A.* **37**, 656

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1929; *C.A.* **26**,

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[illegible]

C.A. **25**, 5678 (1931). (222) Roessler & Hasslacher Chem. Co., French 732,569, Sept. 22, 1932; [illegible] *C.A.* **27**, 2961 (1933)]; [illegible] ur Branntwein), Ger. [illegible] Levine, Cass (to du Pont Co.), Can 396,353, May 6, 1941; *Cent.* **1942**, II 1180; not in *C.A.* (225) Pitman (to du Pont Co), U S. 1,925,602, Sept. 5, 1933, *Cent* **1933**, II 3192; *C.A.* **27**, 5445 (1933). (226) Imperial Chem Ind. Ltd., French 744,128, April 12, 1933, *Cent.* **1933**, II 605; *C.A.* **27**, 3941 (1933). (227) Missbach (to Stauffer Chem. Co), U S 2,043,257–2,043,260, incl., June 9, 1936; *Cent.* **1936**, II 3845; *C.A.* **30**, 5240 (1936). (228) Consortium fur Elektrochem. Ind., French 726,362, May 27, 1932; *Cent.* **1932**, II 1363; *C.A.* **26**, 4829 (1932). (229) Carlisle (to du Pont Co.), U.S. 1,996,717, April 2, 1935; *Cent.* **1935**, II 920, *C.A.* **29**, 3353 (1935). (230) Stewart, DePree (to Dow Chem. Co), U.S. 1,917,073, July 4, 1933, *C.A* **27**, 4539 (1933).

(231) Roessler & Hasslacher Chem. Co , Ger. 562,820, March 3, 1932; *C.A.* **27**, 992 (1933). (232) Dangelmaier (to Roessler & Hasslacher Chem. Co.), U.S. 1,816,895, Aug. 4, 1931; *Cent.* **1931**, [illegible] 1930, *C.A.* **24**, 5309 (1930). (233) [illegible] . **1936**, I 176; *C.A.* **28**, 7383 (1934). [illegible] 378,084, Sept. 1, 1932; *Cent.* **1932**, [illegible] Can. Ind , Ltd.), Can. 341,792, May [illegible] Elektrochem. Ind., French 814,423, June 23, 1937; *Cent.* **1937**, II 3953; *C.A* **32**, 957 (1938): French 51,288, Feb. 18, 1942; *Cent.* **1942**, II 1180: Ger. 721,380, April 30, 1942; [*C.A.* **37**, 4748 (1943)]. (237) Mugdan, Wimmer (to Consortium für Elektrochem Ind.), U S 2,338,297, Jan. 4, 1944; *C.A.* **38**, 3668 (1944); Ger. 736,232, April 29, 1943, *C.A.* **38**, 2972 (1944). (238) Consortium fur Elektrochem. Ind ,

[illegible]

(241) Hopff, Rautenstrauch (to I G.), Ger. 719,914, April 21, 1942; *Cent.* **1942**, II 721; *C.A* **37**, 2104 (1943). [illegible] Müller, Schumacher, *Z. physik. Chem.* [illegible]). (244) Mkryan, Babayan, *Sbornik* [illegible] –58; *C.A.* **37**, 5694 (1943). (245) K[illegible] (246) Hofmann, Kirmreuther, *Ber.* **42**, 4484–4485 (1909). (247) Prins, *Rec. trav. chim.* **45**, 80–81 (1926). (248) Müller, Hönn, *J. prakt Chem* (2) **133**, 289–290 (1932). (249) Kaufler, *Ann.* **433**, 48–51 (1923). (250) Simon, Chavanne, *Compt. rend* **176**, 309–311 (1923); *Bull. soc. chim. Belg.* **32**, 285–287 (1923); *Cent.* **1923**, III 1212; *C.A.* **18**, 1112 (1924).

(251) Simon, Chavanne, U.S. 1,304,108, May 20, 1919; *C.A.* **13**, 2039 (1919): Brit. 129,301, May 21, 1917, *C.A.* **13**, 2878 (1919)· French 22,304, June 30, 1921; *Cent.* **1922**, II 1172. (252) Comp. Prod. Chim. d'Alais, etc., Ger. 359,910, Sept. 28, 1922, *Cent.* **1923**, II 404; not in *C.A.* (253) Comp. Prod. Chim. d'Alais, etc , Ger. 377,524, June 21, 1923; *Cent.* **1923**, IV 536; not in [illegible]

[illegible] 653; not [illegible] to I.G), [illegible] Hunter, [illegible] (263) Con- [illegible] 7, 2836 [illegible] *Ber.* **63**, [illegible] Stephens,

J. Soc. Chem. Ind. **43**, 314–315 (T) (1924). (268)

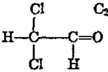
(274) Consortium für Elektrochem. Ind., Ger. 3
in *C.A.* (275) Gowing-Scopes, *Analyst* **39**, 6–7 (1914). (276) Sastry, *J. Soc. Chem. Ind.* **35**, 94–95 (1916). (277) Crudes, *Industria y quím.* **13**, 265–266 (1916); *C.A.* **11**, 544 (1917); not in *Cent.* (278) Griesheim-Elektron A.G., *Chem. Ztg.* **35**, 256 (1911). (279) Elsner, *Chem. Ztg.* **41**, 901–902 (1917). (280) Formanek, *Chem. Obzor* **5**, 57–59 (1930); *Cent.* **1930**, II 976; *C.A.* **24**, 4492 (1930).

(281) Imperial Chem. Industries, *Chem. Trade J.* **93**, 227–229 (1933); *Cent.* **1933**, II 3612. (282) Lenze, M
Dow Chem. Co.
Consortium für
Italian 377,536, Oct. 2, 1939; *Cent.* **1942**, I 2195; not in *C.A.* (285) Goldschmidt, Schüssler, *Ber.* **58**, 566–570 (1925). (286) Steinkopf, Kühnel, *Ber.* **75**, 1327 (1942). (287) Pope, Smith, *J. Chem. Soc.* **119**, 396 (1921). (288) Ruggli, Marszak, *Helv. Chim. Acta* **11**, 180–196 (1928), (289) Böeseken, Bastet, *Rec. trav. chim.* **32**, 203–205 (1913). (290) Prins, *J. prakt. Chem.* (2) **89**, 415, 417, 421 (1914).

(291) Prins, Ger. 261,689, July 2, 1913; *Cent.* **1913**, II 294; *C.A.* **7**, 3641 (1913). (292) Henne, Ladd, *J. Am. Chem. Soc.* **60**, 2494–2495 (1938). (293) Prins, *Rec. trav. chim.* **56**, 120, 123 (1937). (294) Prins, *Rec. trav. chim.* **57**, 659–666 (1938). (295) Prins, *Rec. trav. chim.* **51**, 469–474 (1932). (296) Mead (to Imperial Chem. Ind., Ltd.), Brit. 550,853, Jan. 27, 1943; *C.A.* **38**, 1751 (1944). (297) Roberts (to Imperial Chem. Ind., Ltd.), Brit. 550,854, Jan. 27, 1943; *C.A.* **38**, 1751 (1944). (298) Cusa, McCombie, *J. Chem. Soc.* **1937**, 769–770. (299) Levinstein, Imbert (to British Dyestuffs Corpn.), Brit. 173,540, Feb. 2, 1922; *Cent.* **1922**, IV 760; *C.A.* **16**, 1435 (1922); Ger. 436,620, Nov. 5, 1926; [*Cent.* **1927**, I 181]; not in *C.A.*: French 527,554, Oct. 27, 1921; Swiss 93,576, March 16, 1922; *Cent.* **1922**, IV 761]; not in *C.A.* (300) Wyler (to British Dyestuffs Corpn.), Brit. 188,933, Dec. 14, 1922; *Cent.* **1923**, IV 663; *C.A.* **17**, 1646 (1923); Ger. 437,409,

. **28**, 727 (1934). (306) Doughty, *J. Am.*
, *J. Chem. Soc.* **1938**, 1218–1222. (308)
May 30, 1935; *Cent.* **1936**, I 642; *C.A.* **29**,
0).

3:5180 DICHLOROACETALDEHYDE



$C_2H_2OCl_2$

Beil. I - 613
I_1-(328)
I_2-(677)

B.P. 89.5–90.5° (1)
88–90° (2) (3)
88.4–89.6° (4)
87–88° (5)

Anhydrous C̄ is strongly lachrymatory liq.; in s.t. C̄ can be kept but in open containers it gradually changes to an amorphous polymer, insol. alc. but from which C̄ can be regenerated at 120° (2) cf. (6).

[For prepn. of C̄ from dichloroacetaldehyde diethylacetal (3:6110) by distn. with conc. H_2SO_4 (1) (2) (7) or with benzoic anhydride (1:0595) + a little conc. H_2SO_4 (3) (yield: 81% (5), 78% (8)) see indic. refs.; for prepn. of C̄ from chloral hydrate (3:1270) with Al/Hg see (9); for manufacture of C̄ from chloroform + formaldehyde with SO_2Cl_2 at 300° (10) or with heat, pressure, and cat. (11) see indic. refs.]

[For formn. of C̄ from α,β,β-trichloroethyl ethyl ether (1), β,β-dichlorovinyl methyl (12) or ethyl (1) ethers on htg. with acids; from β,β,β-trichlorolactic acid or its sodium salt by htg. in CO_2 (13) or warming aq. soln. (14) (22), or from its acetate with ethereal Et_3N followed by warming with aq. (13) (15); from ethyl α-ethoxy-β,β-dichloroacrylate on warming with aq. (16); from dichloropyruvic acid by htg. with aq. (15) see indic. refs.]

[For formn. of C̄ from acetylene with HOCl (17) or from chloroacetylene (3:7000) with NaOCl (18) see indic refs.]

C̄ in pres. of conc. H_2SO_4 polymerizes (19) to a cryst. tri (?) mer paradichloroacetaldehyde, m p. 129–130° (19), and eas. sol. alc.; this prod. on htg. in a s.t. at 240–245° or with conc. H_2SO_4 at 120–130° regenerates C̄. [For use of C̄ and this polymer as insecticides see (20).]

C̄ with 1 mole aq. and cooling yields (1) dichloroacetaldehyde hydrate (3:1085), m.p. 56°.

C̄ with abs. EtOH yields (1) dichloroacetaldehyde monoethylacetal (dichloroacetaldehyde ethyl alcoholate) (3:5310). [For dichloroacetaldehyde diethylacetal, b.p. 184° see 3.6110.]

C̄ reduces $NH_4OH/AgNO_3$. — C̄ on oxidn. with fumg. HNO_3 yields (21) dichloroacetic acid (3:6208).

[C̄ with PCl_5 yields (22) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (which if much HCl is present may be accompanied by $\alpha,\beta,\beta,\alpha',\beta',\beta'$-hexachlorodiethyl ether (22)).]

C̄ with 1 mole $NH_2OH.HCl$ in aq. soln. yields (23) a liquid oxime, b.p. 67–69° at 17 mm., 40–44° at 2–3 mm dec ; however, with excess $NH_2OH.HCl + Na_2CO_3$ C̄ yields (14) (16) glyoxal dioxime [Beil I-761, I_1-(394), I_2-(818), m p. 177–178° (16), 173° (14).

C̄ with excess phenylhydrazine yields (24) (25) glyoxal *bis*-phenylosazone, pale yel. pl. from boilg. alc., m.p. 169–171° (25), 170° (24).

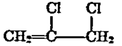
C̄ with 1 mole semicarbazide in alc. yields (26) dichloroacetaldehyde semicarbazone, m p. 155–156° (26); C̄ with 2 moles semicarbazide in aq. soln. gives on boilg. (26) glyoxal *bis*-semicarbazone, insol. in usual solvents and not melting below 270° (27).

3:5180 (1) Oddo, Mameli, *Gazz. chim. ital.* **33**, II 388–412 (1903). (2) Paterno, *Zeit für Chemie* **1868**, 667. (3) Wohl, Roth, *Ber.* **40**, 217 (1907). (4) Cheng, *Z. physik. Chem.* **B-26**, 295 (1934). (5) van de [illegible]
Ann. **206**, 252 (1880). [illegible]
Tellegen, Plusje, *Rec. tr* [illegible]
(1934). (10) Standard [illegible]
C.A. **30**, 6006 (1936).

(11) Frolich, Wiezevich (to St [illegible], 1936; *Cent* **1936**, II 3193; *C.A.* **30**, 487 [illegible] (13) Koetz, *J. prakt. Chem.* (2) **90**, 3 [illegible] (15) Koetz, Otto, *J. prakt Chem.* (2) [illegible] **103**, 235 (1921/22). (17) Wittorf, *J. Russ. Phys -Chem. Soc.* **32**, 88–117 (1900); *Cent.* **1900**, II 29. (18) Ingold, *J. Chem. Soc* **125**, 1536–1537 (1924). (19) Jacobsen, *Ber.* **8**, 87–88 (1875). (20) Ger. 528,194, June 26, 1931; *Cent.* **1931**, II 1910.

(21) Paterno, *Zeit. für Chemie* **1869**, 394. (22) Paterno, Pisati, *Gazz. chim. ital* **1**, 463 (1871). (23) Routala, Neovius, *Ber.* **57**, 252–254 (1924). (24) Oddo, Cusmano, *Gazz chim. ital.* **41**, II 255 (1911) (25) Chattaway, Farinholt, *J. Chem. Soc.* **1930**, 96 (26) Kling, *Bull. soc. chim.* (4) **5**, 414–415 (1909). (27) Harries, Temme, *Ber.* **40**, 171 (1907).

3:5190 2,3-DICHLOROPROPENE-1 (β-Chloroallyl chloride)



$C_3H_4Cl_2$ Beil. I-199, I_1—, I_2—

B.P. 94–94.5° (1) (6)
94° (2) (3)
92.5° (4)

$D^{25}_{25} = 1.204$ (3) $n^{21}_D = 1.4600$ (5)

Colorless oil, insol. aq., sol. alc., ether.

[For prepn. of C̄ from 1,2,3-trichloropropane (3:5840) + aq. alk. (yield 80% (5), 87% (4), 70% (1)) or alc. alk. (4) see indic. refs.; for other misc. methods of formn. see Beil. I-199.]

C̄ shaken with 6–7 pts. conc. H_2SO_4, poured into aq., and distd. yields (7) chloroacetone (3:5425), b.p. 118°.

C̄ adds Br_2 giving (3) 2,3-dichloro-1,2-dibromopropane [Beil. I-112], b.p. 205° (3).

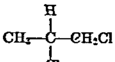
C̄ htd. with fumg. HCl in s.t. at 100° yields (3) 1,2,2-trichloropropane (3:5475), b.p. 123°.

[For study of addn. of HF see (4).]

[For use of C̄ in prepn. of cellulose ethers with unsatd. linkages see (8).]

3:5190 (1) Bon, *Uchenye Zapiski Leningrad. Gosudarst. Univ., Ser. Khim. Nauk.* **3**, 3–37 (1938); *Cent.* **1939**, II 366. (2) Kirmann, *Bull. soc. chim.* (5) **6**, 846 (1939). (3) Friedel, Silva, *Jahresber.* **1871**, 404; **1872**, 322–323. (4) Henne, Haeckl, *J. Am. Chem. Soc.* **63**, 2692–2694 (1941). (5) Hurd, Webb, *J. Am. Chem. Soc.* **58**, 2191 (1936). (6) Claus, *Ann.* **170**, 126 (1874). (7) Henry, *Ber.* **5**, 190–191 (1872). (8) du Pont Co., Brit. 429,949, July 11, 1935; *Cent.* **1936**, I 4098.

3:5200 *d,l*-1,2-DICHLOROPROPANE (Propylene (di)chloride)



$C_3H_6Cl_2$ Beil. I-105, I_1—, I_2-(73)

B.P. 96.8° at 760 mm. (1) (2)
96.4–96.6° (3) (4) (5)
96.4° at 760 mm. (6)
95.2–96.0° at 760 mm. (7) (8)

$D^{20}_4 = 1.1545$ (6) $n^{20}_D = 1.4388$ (9)

Colorless oil. — For b.p.'s at various pressures from 33–847 mm. see (6) (10). — Almost insol. in aq.; for precise data see (3) (4) (5). — [For use as technical solvent see (11); for use in concn. of AcOH by formn. with aq. of const.-boilg. mixt., b.p. 96° see (12).]

[For prepn. of C̄ from corresp. alc., propanediol-1,2 (propylene glycol) (1:6455), with $PCl_3 + ZnCl_2$ (13% yield (13)), or $PCl_5 + ZnCl_2$ (11% yield (13)), or $SOCl_2$ (15% yield (13)), or $SOCl_2$ + pyridine (28% yield (13)), see (13); for prepn. of C̄ from propylene by addn. of Cl_2 (88% yield (9)) see (9) (14) (30); for formn. of C̄ (35.6% (15)) together with other products by chlorination of propane (15) (16) (17) see indic. refs.; for formn. of C̄ (60% (18)) together with 1,3-dichloropropane (3:5450) (40% (18)) from 1-chloropropane (3:7040) with SO_2Cl_2 see (18); for other misc. methods see Beil. I-105.]

[For study of limits of inflammability (3.4%–14.5% by volume) of C̄ in air see (19); for study of thermal conductivity of C̄ see (20); for adsorption of C̄ by activated carbon at various temps. see (31).]

C̄ on further chlorination with SO_2Cl_2 yields (18) cf. (32) 48% 1,2,2-trichloropropane (3:5475), 37% 1,2,3-trichloropropane (3:5840) cf. (21), and 15% 1,1,2-trichloropropane (3:5630).

$\bar{C}$ on htg. at 540–750°C. loses HCl yielding (15) (22) a mixt. of 3-chloropropene-1 (allyl chloride) (3:7035) and 1-chloropropene-1 (3:7030). — $\bar{C}$ with aq. alk. under pressure and above b.p. of $\bar{C}$ yields (23) 2-chloropropene-1 (isopropenyl chloride) (3:7020). — $\bar{C}$ with alc. KOH (but not NaOH (9)) at 60–75° gives (95% yield (9)) mixt. of 2-chloropropene-1 (3:7020) and 1-chloropropene-1 (3:7030) cf. (21) (28).

[For reactn. of $\bar{C}$ with salts of lower aliphatic acids yielding esters of *d,l*-propylene glycol (1:6455) see (24); with conc. aq. NH_4OH at 78–80° giving (92% yield (25)) propylenediamine dihydrochloride and other products (26) see indic. refs.]

$\bar{C}$ htd. with aq. + PbO in s t. at 150° is said [Beil. I-105] to yield *d,l*-propylene glycol (1.6455), but $\bar{C}$ htd. with 20 vols. aq. in s.t. at 210–220° yields (2) from the glycol a mixt. of propionaldehyde (1:0110) and acetone (1:5400). — [For behavior of $\bar{C}$ with boilg. aq. + trace of $NaHCO_3$, or with boilg. aq. + Fe, see (15).]

—— **1,2-Diphenoxypropane:** m.p. 32°, b.p. 175–178° at 12 mm. (27). [From 1-bromo-2-phenoxypropane with 25% alc. $NaOC_6H_5$ (27); it has not, however, been reported direct from $\bar{C}$.]

—— **1,2-Di(α-naphthoxy)propane:** unrecorded.

—— **1,2-Di-(β-naphthoxy)propane:** m.p. 152° (29). [From $\bar{C}$ with β-naphthol (1:1540) + aq NaOH in s.t. at 120° (29).]

3:5200 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* **28**, 338 (1936). (2) Linnemann, *Ann.* **161**, 62–64 (1872). (3) Gross, *Physik. Z.* **32**, 589 (1931). (4) Gross, *Z. physik. Chem* **B-6**, 215–220 (1929). (5) Gross, *J. Am. Chem. Soc.* **51**, 2362–2366 (1929) (6) Nelson, Young, *J. Am. Chem. Soc* **55**, 2429–2433 (1933). (7) Kahovec, Wagner, *Z. physik. Chem.* **B-47**, 52 (1940). (8) Kohlrausch, Ypsilanti, *Z. physik. Chem.* **B-32**, 416 (1936). (9) Goudet, Schenker, *Helv. Chim. Acta* **10**, 132–137 (1927). (10) Kireev, Nikiforova, *J. Gen. Chem.* (*U.S S.R.*) **6**, 75–77 (1936); *Cent.* **1937**, I 4219; *C.A.* **30**, 7427 (1936).

(11) Durrans, "Solvents," 4th ed , London, 1938, p. 182. (12) Othmer (to Eastman Kodak Co), U S. 2,021,852, Nov. 19, 1935; *Cent.* **1936**, I 1505. (13) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (14) Union Carbide Co., Ger. Pat 363,269, Nov. 6, 1922; *Cent.* **1923**, II 475–476. (15) McBee, Hass, Chao, Welch, Thomas, *Ind. Eng. Chem.* **33**, 176–181

(21) Klebanskii, Vol'kenshtein, *J. Applied Chem.* (*U.S S R.*) **8**, 106–116 (1935); *Cent.* **1935**, II 3298. (22) Essex, Ward, U S. 1,477,047, Dec. 11, 1923; *C.A.* **18**, 537 (1924). (23) Young (to Carbide and Carbon Chem. Corp), U S 1,752,049, March 25, 1930; *Cent.* **1930**, II 1280. (24) Coleman, Moore (to Dow Chem. Co), U S. 2,021,852, Nov. 19, 1935; *Cent* **1936**, I 1505. (25) Darzens, *Compt. rend* **208**, 1503–1504 (1939), *C.A* **33**, 6243 (1939). (26) Mnookin, U.S. 2,049,467, August 4, 1936, *Cent.* **1937**, I 1792. (27) Gilta, *Bull. soc. chim. Belg.* **31**, 249 (1922) (28) Reboul, *Ann. chim.* (5) **14**, 462–464 (1878). (29) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144, Oct. 30, 1934; *Cent.* **1935** I 3051; [*C A.* **29**, 177 (1935)]. (30) Gavat, *Ber.* **76**, 1115–1118 (1943).

(31) Pearce, Eversole, *J. Phys. Chem.* **38**, 383–393 (1934). (32) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945, *C.A.* **39** 3534 (1945).

3:5210 TRICHLOROACETALDEHYDE $Cl_3C.CHO$ C_2HOCl_3 Bell. I - 616
(Chloral) I_1-(328)
I_2-(677)

B.P.			F.P.		
97.8–98.1°		(1)	−57.5° (9)	D_4^{25} = 1.5060 (1) cf. (19)	
97.75°	at 760 mm.	(2)		1.5049 (15) (19)	
97.73°	at 760 mm.	(3)		1.5030 (9) cf. (19)	
97.7°		(4)		1.4730 (5)	
97.4–97.6°	at 768 mm.	(5) (19)		$D_4^{21.4}$ = 1.5059 (16)	$n_{He}^{21.4}$ = 1.45412 (16)
97.2°	cor. at 760 mm.	(6)			
				D_4^{20} = 1.5121 (10)	n_D^{20} = 1.4568 (17)
97.2°	at 731.3 mm.	(7)		1.508 (16)	1.4559 (14)
97°	at 747 mm.	(8)		1.5066 (14)	1.45572 (10)
97°	at 740 mm.	(9)		See also Note 2.	
96–97°	at 750 mm.	(10)			n_{He}^{20} = 1.4548 (16)
96.5–96.9°		(11)			
96.5°		(12) (13)			
96.4°	at 749 mm.	(14)			
See also Note 1.					

Note 1. For vapor press. of C̄ between 0° and 30° see (18).

Note 2. For D_4^t over range 25–85° see (15).

[*See also chloral hydrate* (3:1270) *and chloral ethylalcoholate* (3:0860).]

Important note: The chemistry of anhydrous chloral on one hand and that of chloral hydrate on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. For instance, there are many reactions actually employing chloral hydrate as the starting point, which by virtue of the simultaneous use of conc. H_2SO_4 are undoubtedly in effect reactions of anhydrous chloral. In such cases the allocation of text between the two entries has been influenced by the nature and magnitude of the context. Although cross references have been liberally employed, the texts of both anhydrous chloral and of chloral hydrate should be compared.

MISCELLANEOUS PHYSICAL PROPERTIES

Binary systems contg. C̄. C̄ with H_2O combines to give chloral hydrate (3:1270) q.v. (for use in this reaction of C̄ in effecting drying of halogen compounds used in fire extinguishers see (20)); for extensive study of system C̄ + aq. see (9).

C̄ with EtOH (1:6130) combines to give chloral ethylalcoholate (3:0860) q.v.— For analogous reactions of C̄ with other alcs. see below under chemical behavior of C̄.

Azeotropic mixtures containing C̄. A few such systems are known including the following: C̄ with methylcyclohexane (hexahydrotoluene) (1:8410) gives a const.-boilg. mixt., b.p. 94.45° at 760 mm., contg. 57% C̄ (2); C̄ with isobutyl formate (1:3065) gives a const.-boilg. mixt., b.p. 100.1° at 760 mm., contg. 60% C̄ (21); C̄ with *n*-propyl acetate (1:3075) gives a const.-boilg. mixt., b.p. 102.55° at 760 mm., contg. 50.5% C̄ (21); C̄ with nitromethane gives a const.-boilg. mixt., b.p. 93° at 760 mm., contg. 65% C̄ (20).

PREPARATION OF C̄

From Halogen-Free Starting Points

From ethyl alcohol. [C̄ was first prepared (22) from EtOH (1:6130) by action of Cl_2; for discussion of mechanism of reaction see (23) (24); note that various by-products (25) (26) such as 1,1-dichloroethane (3:5035), 1,2-dichloroethane (3:5130), 1,1,2-trichloroethane (3:5330), β,β,β-trichloroethanol (3:5775), ethyl dichloroacetate (3:5850), and chloroform

(3:5050) have been detected; for patents on prepn. of C̄ (or its hydrate) from EtOH with Cl_2 see (27) (28); for use of Cl_2 in pres. of $FeCl_3$ see (29).]

From acetaldehyde. [For prepn. of C̄ from acetaldehyde (1:0100) with Cl_2 see (30) (31).]

From other non-halogenated materials. [For formation of C̄ from ethyl formate (1:3000) with SO_2Cl_2 in s t. at 170° (32) or from starch or sucrose by distn. with MnO_2 + HCl (33) see indic. refs.]

FROM HALOGENATED STARTING MATERIALS

From chloro-unsaturates. [For formn. of C̄ from 1,1,2-trichloroethylene (3:5170) with large excess Cl_2O in CCl_4 at −20° (34) or on oxidn. in pres. of $FeCl_3$, $AlCl_3$, $TiCl_4$, or $SbCl_3$ as directed (35) see indic. refs.; from chloroacetylene (3:7000) with aq. 30% NaOCl + H_3BO_3 see (36).]

From carbon tetrachloride. [For prepn. of C̄ from CCl_4 (3·5100) with formaldehyde + SO_2Cl_2 + cat. at high temp. (200–500°) and high press. (20–200 atm.) see (401).]

From various chloral derivatives. [For prepn of C̄ from chloral hydrate (3:1270) by dehydration with conc. H_2SO_4 (note that C̄ is appreciably soluble in conc. H_2SO_4 (9)) or with CaC_2 slowly in cold but rapidly at 100° (37); from chloral ethylalcoholate (3:0860) (or other chloral alcoholates) with conc. H_2SO_4, from chloral polymers such as "metachloral" by htg at 180–200° (38); from trichloroacetaldehyde diethylacetal ("trichloroacetal") (3:6317) above 200° (39) or on distn with conc. H_2SO_4 (39) (40); from dichloroacetaldehyde diethylacetal ("dichloroacetal") (3:6110) with Cl_2 at 60–70° (41) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄ WITH INORGANIC REACTANTS

GENERAL

[For review of chemistry of C̄ and its hydrate (3:1270) see (42).]

REDUCTION OF C̄

According to the nature of the reagent and the conditions, C̄ (or its hydrate) may undergo reduction either at its $-CCl_3$ group or at its —CHO group.

Reduction at $-CCl_3$ group [C̄ with H_2 + Pd in alc. KOH (43) or with H_2 + Ni + aq. alk. (44) splits off all its halogen as HCl. — C̄ with Zn + AcOH (45) (46), with Al + AcOH (75), with Zn + strong HCl (47) (48), with Zn + dil. H_2SO_4 (49) (50), reduces to acetaldehyde (1:0100); because of easy volatility of this product the reaction may be used for the identification and detection of C̄ (47) (49) (50), or for detection of C̄ in presence of $CHCl_3$ (3·5050) or of α,α,β-trichloro-n-butyraldehyde ("butyrchloral") (3:5910) (49). — Note that C̄ with aq. Zn or Fe powder especially on warming gives (51) CH_4 + MeCl (3:7005) + CH_2Cl_2 (3:5020).]

[C̄ in aq. with Al/Hg gives (52) dichloroacetaldehyde hydrate (3:1085), while C (as hydrate) on electrolytic reduction (53) gives dichloroacetaldehyde (3:5180) + chloroacetaldehyde (3:7212) + acetaldehyde (1:0100).]

Reduction at —CHO group. [C̄ with $Al(OEt)_3$ in abs. EtOH gives (yields: 85% (54), 84% (55), 80% (56)) (57) (58) (59) cf. (60) 2,2,2-trichloroethanol-1 (3:5775); for reduction of C̄ to this same product using Al isopropylate in isopropyl alc. (61) in pres. of acetaldehyde (yield 72–87% (62)), C_2H_5OMgBr (63), $(CH_3)_2CHOMgBr$ (63), or other metallic isopropylates (64), $ZnEt_2$ (65) (66), $AlEt_3$ compd. with ether (88 5% yield (67)) (note, however, that $SnEt_4$ is not effective (67)), or fermenting yeast (68) (69), see indic. refs. — For formn. of 2,2,2-trichloroethanol-1 (3:5775) during reaction of C̄ with various RMgX compounds see below under behavior of C̄ with RMgX cpds.]

3:5210 TRICHLOROACETALDEHYDE $Cl_3C.CHO$ C_2HOCl_3 Beil. I - 616
(Chloral) I_1-(328)
I_2-(677)

B.P.			F.P.		
97.8–98.1°		(1)	−57.5° (9)	D_4^{25} = 1.5060 (1) cf. (19)	
97.75°	at 760 mm.	(2)		1.5049 (15) (19)	
97.73°	at 760 mm.	(3)		1.5030 (9) cf. (19)	
97.7°		(4)		1.4730 (5)	
97.4–97.6°	at 768 mm.	(5) (19)		$D_4^{21.4}$ = 1.5059 (16)	$n_{He}^{21.4}$ = 1.45412 (16)
97.2°	cor. at 760 mm.	(6)			
				D_4^{20} = 1.5121 (10)	n_D^{20} = 1.4568 (17)
97.2°	at 731.3 mm.	(7)		1.508 (16)	1.4559 (14)
97°	at 747 mm.	(8)		1.5066 (14)	1.45572 (10)
97°	at 740 mm.	(9)		See also Note 2.	
96–97°	at 750 mm.	(10)			n_{He}^{20} = 1.4548 (16)
96.5–96.9°		(11)			
96.5°		(12) (13)			
96.4°	at 749 mm.	(14)			
See also Note 1.					

Note 1. For vapor press. of C̄ between 0° and 30° see (18).
Note 2. For D_4^t over range 25–85° see (15).

[*See also chloral hydrate* (3:1270) *and chloral ethylalcoholate* (3:0860).]

Important note: The chemistry of anhydrous chloral on one hand and that of chloral hydrate on the other is so closely interwoven that the division of material between them in this book is necessarily arbitrary. For instance, there are many reactions actually employing chloral hydrate as the starting point, which by virtue of the simultaneous use of conc. H_2SO_4 are undoubtedly in effect reactions of anhydrous chloral. In such cases the allocation of text between the two entries has been influenced by the nature and magnitude of the context. Although cross references have been liberally employed, the texts of both anhydrous chloral and of chloral hydrate should be compared.

MISCELLANEOUS PHYSICAL PROPERTIES

Binary systems contg. C̄. C̄ with H_2O combines to give chloral hydrate (3:1270) q.v. (for use in this reaction of C̄ in effecting drying of halogen compounds used in fire extinguishers see (20)); for extensive study of system C̄ + aq. see (9).

C̄ with EtOH (1:6130) combines to give chloral ethylalcoholate (3:0860) q.v.—For analogous reactions of C̄ with other alcs. see below under chemical behavior of C̄.

Azeotropic mixtures containing C̄. A few such systems are known including the following: C̄ with methylcyclohexane (hexahydrotoluene) (1:8410) gives a const.-boilg. mixt., b.p. 94.45° at 760 mm., contg. 57% C̄ (2); C̄ with isobutyl formate (1:3065) gives a const.-boilg. mixt., b.p. 100.1° at 760 mm., contg. 60% C̄ (21); C̄ with *n*-propyl acetate (1:3075) gives a const.-boilg. mixt., b.p. 102.55° at 760 mm., contg. 50.5% C̄ (21); C̄ with nitromethane gives a const.-boilg. mixt., b.p. 93° at 760 mm., contg. 65% C̄ (20).

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(3:5050) have been detected; for patents on prepn. of $\bar{C}$ (or its hydrate) from EtOH with Cl_2 see (27) (28); for use of Cl_2 in pres. of $FeCl_3$ see (29).]

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CHEMICAL BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

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Oxidation of $\bar{C}$

$\bar{C}$ or its hydrate (3:1270) on oxidation under appropriate conditions gives trichloroacetic acid (3:1150); under some circumstances extensive decompn. also occurs (see below).

[$\bar{C}$ on oxidn. with fumg. HNO_3 (70) cf. (71), with HNO_2 (72), with NO_2 at 40–60° (70% yield (73)) or with aq. chlorates + cat. (74) gives trichloroacetic acid (3:1150); for formn. of latter as by-product of action of $\bar{C}$ with O_2 including comments on inhibitors, etc., see (38) (75).]

[Chloral hydrate (3:1270) on oxidn. with fumg. HNO_3 (63% yield (76)) cf. (72), with $KMnO_4$ (77) (80), with $KClO_3$ (78), with aq. chlorates + cat. (74), or with $Ca(OCl)_2$ (79) gives trichloroacetic acid (3:1150).]

Chloral hydrate (3:1270) reduces $NH_4OH/AgNO_3$ (81) or Fehling's soln. (for study of sensitivity of this reaction see (82) [for oxidn. of chloral hydrate by HgO, $KMnO_4$, or CrO_3 see (83); for reduction by chloral hydrate of AgCl, AgBr, AgI, or AgSCN to metallic silver (84) or of alkaline solns. of Au, Ag, Bi, and Cu salts (85) see indic. refs.].

[$\bar{C}$ in dry C_6H_6 is but slowly attached by silver oxide (86).]

Reactions Involving Decomposition of $\bar{C}$

(See also below under behavior of $\bar{C}$ with alkalies.)

[$\bar{C}$ with aq. HIO_3 at 100° decomposes yielding (87) $CHCl_3$ (3:5050) + CO_2 + ICl_3 + I_2. — $\bar{C}$ on chlorine-sensitized (88) or bromine-sensitized (12) photochemical oxidn. with O_2 at 70–90° decomposes yielding (88) (12) $COCl_2$ (3:5000) + CO + HCl.]

[$\bar{C}$ on thermal decompn. at about 440°C. especially if catalyzed by I_2 (89) or NO (89) (90) gives $CHCl_3$ (3:5050) + CO.]

[$\bar{C}$ with $AlCl_3$ on htg. gives various products according to conditions; these include tetrachloroethylene (3:5460) (91) (92), pentachloroethane (3:5880) (93), $\alpha,\alpha,\beta,\beta,\gamma,\gamma,\gamma$-heptachloro-*n*-butyraldehyde ("perchlorobutanal") (94), chloral polymers (especially metachloral (91) (92) (95)), chloralide (3:3510) (92) (94), and others.]

Behavior of $\bar{C}$ with Halogens

With chlorine. [$\bar{C}$ with Cl_2 in sunlight decomposes giving (96) CCl_4 (3:5100) + $COCl_2$ (3:5000) + HCl; for extensive study of photochem. reaction of $\bar{C}$ with Cl_2 at 70–90° giving CCl_4 (3:5100) + CO + HCl see (97). — Note that $\bar{C}$ with Cl_2, Br_2, or I_2 in pres. of $AlCl_3$ gives (98) hexachloroethane (3:4835).]

With bromine. [$\bar{C}$ with Br_2 at 150° gives (99) trichloroacetyl bromide + bromotrichloromethane + CO + HBr; for extensive study of photochem. reaction of $\bar{C}$ with Br_2 at 70–90° giving bromotrichloromethane, $CHCl_3$ (3:5050), $COBr_2$, CO + HBr see (13).]

Behavior of $\bar{C}$ with Inorganic Acids

$\bar{C}$ with inorganic acids reacts in various ways according to circumstances; e.g., by formn. of addn. products, by decomposition, by formation of chloralide, by polymerization (see also its own heading below), or by combinations of these reactions.

With HCl. [$\bar{C}$ with HCl gas at −15 to −75° yields (100) (113) an addn. product $\bar{C}$.HCl commonly designated as chloral hydrochloride; this crystn. product with aq. dissociates giving $\bar{C}$ (as hydrate) + HCl; note that little, if any, polymerization occurs (100).]

With HBr. [$\bar{C}$ with HBr gas at −15° yields (100) an addn. prod.; C.HBr, similar in behavior to that of the preceding HCl addn. product.]

With HNO_3. [$\bar{C}$ with HNO_3 at 20° yields (101) an addition prod., $C.HNO_3$.]

With H_2SO_4. [$\bar{C}$ with fumg. H_2SO_4 contg. 2% SO_3 gives on warming substantially 100% yields (102) of chloralide (3:3510); note, however, that $\bar{C}$ with fumg. H_2SO_4 contg.

10% SO_3 gives at 0° an addn. prod. of the type $C_m\ (SO_3)_n.(H_2O)_p$ which on warming dec. giving $COCl_2$ (3:5000) + SO_2Cl_2 + SO_2 + CO_2 + CO + HCl (102); for other (older) refs. on conversion of C̄ with fumg. H_2SO_4 to chloralide (3:3510) see (61) (81) (103) (104); for conversion of chloral hydrate (3:1270) with fumg. H_2SO_4 to chloralide (3:3510) (yields 61% (105), 44–51% (106)) see indic. refs. — Note, however, that within a narrow range of strength (best about 79.8%) H_2SO_4 appears to give with C̄ or its hydrate certain unstable addition products of type $CCl_3.CH(OH).SO_2OH.H_2O$ (148).]

With $ClSO_3H$. [C̄ with chlorosulfonic acid at 50° for several days gives (65% yield (107)) *bis*-(α,β,β,β-tetrachloroethyl) ether (3:0738); note that even at −50° for 10–12 hrs. yield of this prod. may be as high as 50%; also that various other products including chloralide (3:3510) are also formed; and finally that C̄ with FSO_3H behaves similarly (107).]

Polymerization of C̄

C̄ is known to give at least three polymers; the oldest and most common polymer is that designated as "metachloral"; in addition two isomeric α- and β-"parachlorals" (possibly comprising a pair of *cis-trans* stereomers) have also been reported (108).

Metachloral. [C̄ in presence of H_2SO_4 below 0° (108) (sometimes suddenly cf. (109)), fumg. H_2SO_4 (18), pyridine (18), or $AlCl_3$ as directed (18) (92) (110) gives metachloral [Beil. I-618, I_1-(329), I_2-(680)], a white amorphous polymer of unknown mol. wt. or structure. This polymer is insol. aq , alc., ether, or acids but dissolves in aq. Na_2CO_3 forming chloral hydrate (3:1270), on distn. at 180° regenerates C̄, oxidizes with HNO_3 to trichloroacetic acid, with alkalies behaves like C̄ (see also below), and with $ClSO_3H$ at 50° gives (107) *bis*-(α,β,β,β-tetrachloroethyl) ether (3·0738).]

Parachloral. [C̄ with a large excess conc. H_2SO_4 at 15–20°, carefully dissolved and stood 3 days at 15–20°, gives in addn. to metachloral (above) and chloralide (3:3510) small amts. of two isomeric trimers, viz., α-parachloral, rhombs from hot alc , m.p. 116°, b.p. 223° at 760 mm., and β-parachloral, pr. from alc., m.p. 152°, b.p. 250°. Note that yield of parachloral is only about 1% of original C̄, that both are more sol. in hot alc. than the main prod. metachloral, that neither form is convertible to the other or to metachloral, and that both on distn. at ord. press. dissociate to C̄.]

Mixed polymers. [C̄ (1 mole) with acetaldehyde (3 moles) + HCl gas at 0° for 15–20 hrs. gives (78% yield (111)) 2,4-dimethyl-6-(trichloromethyl)-1,3,5-trioxane, b.p. 97° at 13 mm., $D_4^{15} = 1.3915$, $n_D^{18} = 1.4708$. Similar mixed polymers (presumably analogous to the preceding case) are similarly formed (112) from C̄ with trimethylacetaldehyde (1:0133), C̄ with propionaldehyde (1:0110), and C̄ with isobutyraldehyde (1:0120).]

Behavior of C̄ with alkalies. C̄ with conc. aq. alkalies (even in cold (22)), or C̄ on distn. with aq. alkalies or alk. earths (22) (114) (115), undergoes cleavage into $CHCl_3$ (3:5050) + the corresp. salt of formic acid (1:1005); this cleavage is claimed to occur also even with conc. NH_4OH (114) or aq. amines (114) and may also produce some CO (114) and chloride ion. — [For extensive studies of kinetics of this cleavage see (116) (117) (118) (119) (120) (121) (122) (126).]

Note that C̄ is very stable toward hydrolysis by aq. (126) (even in s.t. at 190–200° for 2 hrs. (118)) or by dilute acid (even in s.t. at 150° (118)); however, C̄ with aq. in sunlight is claimed (123) to give formaldehyde (1:0145) + CO_2 + HCl (presumably by formn. and decompn. of $OCH.C(OH)_3$), and C with aq. is claimed (124) to undergo slight formn. of dichloroacetic acid (3:6208) + HCl.

C̄ with alc. KOH gives (125) $CHCl_3$ (3:5050) + ethyl formate (1:3000).

[Note that chloral deuterate, $CCl_3CH(OD)_2$ (from C̄ + D_2O), with NaOD (17) or $Ca(OD)_2$ (127) in D_2O gives deuteriochloroform, $CDCl_3$, b.p. 0.5° higher than ord. $CHCl_3$

Oxidation of $\bar{C}$

$\bar{C}$ or its hydrate (3:1270) on oxidation under appropriate conditions gives trichloroacetic acid (3:1150); under some circumstances extensive decompn. also occurs (see below).

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[$\bar{C}$ with $AlCl_3$ on htg. gives various products according to conditions; these include tetrachloroethylene (3:5460) (91) (92), pentachloroethane (3:5880) (93), $\alpha,\alpha,\beta,\beta,\gamma,\gamma,\gamma$-heptachloro-$n$-butyraldehyde ("perchlorobutanal") (94), chloral polymers (especially metachloral (91) (92) (95)), chloralide (3:3510) (92) (94), and others.]

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With HNO_3. [$\bar{C}$ with HNO_3 at 20° yields (101) an addition prod., $C.HNO_3$.]

With H_2SO_4. [$\bar{C}$ with fumg. H_2SO_4 contg. 2% SO_3 gives on warming substantially 100% yields (102) of chloralide (3:3510); note, however, that $\bar{C}$ with fumg. H_2SO_4 contg.

10% SO_3 gives at 0° an addn. prod. of the type $C_m(SO_3)_n.(H_2O)_p$ which on warming dec. giving $COCl_2$ (3.5000) + SO_2Cl_2 + SO_2 + CO_2 + CO + HCl (102); for other (older) refs. on conversion of $\bar{C}$ with fumg. H_2SO_4 to chloralide (3:3510) see (61) (81) (103) (104); for conversion of chloral hydrate (3:1270) with fumg. H_2SO_4 to chloralide (3:3510) (yields: 61% (105), 44–51% (106)) see indic. refs. — Note, however, that within a narrow range of strength (best about 79.8%) H_2SO_4 appears to give with $\bar{C}$ or its hydrate certain unstable addition products of type CCl_3 CH(OH).SO_2OH.H_2O (148).]

With $ClSO_3H$. [$\bar{C}$ with chlorosulfonic acid at 50° for several days gives (65% yield (107)) *bis*-(α,β,β,β-tetrachloroethyl) ether (3:0738); note that even at −50° for 10–12 hrs. yield of this prod. may be as high as 50%; also that various other products including chloralide (3:3510) are also formed; and finally that $\bar{C}$ with FSO_3H behaves similarly (107).]

Polymerization of $\bar{C}$

$\bar{C}$ is known to give at least three polymers; the oldest and most common polymer is that designated as "metachloral"; in addition two isomeric α- and β-"parachlorals" (possibly comprising a pair of *cis-trans* stereomers) have also been reported (108).

Metachloral. [$\bar{C}$ in presence of H_2SO_4 below 0° (108) (sometimes suddenly cf. (109)), fumg. H_2SO_4 (18), pyridine (18), or $AlCl_3$ as directed (18) (92) (110) gives metachloral [Beil. I-618, I_1-(329), I_2-(680)], a white amorphous polymer of unknown mol. wt. or structure. This polymer is insol. aq., alc., ether, or acids but dissolves in aq. Na_2CO_3 forming chloral hydrate (3:1270), on distn. at 180° regenerates $\bar{C}$, oxidizes with HNO_3 to trichloroacetic acid, with alkalies behaves like $\bar{C}$ (see also below), and with $ClSO_3H$ at 50° gives (107) *bis*-(α,β,β,β-tetrachloroethyl) ether (3:0738).]

Parachloral. [$\bar{C}$ with a large excess conc. H_2SO_4 at 15–20°, carefully dissolved and stood 3 days at 15–20°, gives in addn. to metachloral (above) and chloralide (3:3510) small amts. of two isomeric trimers, viz., α-parachloral, rhombs from hot alc., m.p. 116°, b.p. 223° at 760 mm., and β-parachloral, pr. from alc., m.p. 152°, b.p. 250°. Note that yield of parachloral is only about 1% of original $\bar{C}$, that both are more sol. in hot alc. than the main prod. metachloral, that neither form is convertible to the other or to metachloral, and that both on distn. at ord. press. dissociate to $\bar{C}$.]

Mixed polymers. [$\bar{C}$ (1 mole) with acetaldehyde (3 moles) + HCl gas at 0° for 15–20 hrs. gives (78% yield (111)) 2,4-dimethyl-6-(trichloromethyl)-1,3,5-trioxane, b.p. 97° at 13 mm., $D_4^{16} = 1.3915$, $n_D^{15} = 1.4708$. Similar mixed polymers (presumably analogous to the preceding case) are similarly formed (112) from $\bar{C}$ with trimethylacetaldehyde (1:0133), $\bar{C}$ with propionaldehyde (1:0110), and $\bar{C}$ with isobutyraldehyde (1:0120).]

Behavior of $\bar{C}$ with alkalies. $\bar{C}$ with conc. aq. alkalies (even in cold (22)), or $\bar{C}$ on distn. with aq. alkalies or alk. earths (22) (114) (115), undergoes cleavage into $CHCl_3$ (3:5050) + the corresp. salt of formic acid (1:1005); this cleavage is claimed to occur also even with conc. NH_4OH (114) or aq. amines (114) and may also produce some CO (114) and chloride ion. — [For extensive studies of kinetics of this cleavage see (116) (117) (118) (119) (120) (121) (122) (126).]

Note that $\bar{C}$ is very stable toward hydrolysis by aq. (126) (even in s.t. at 190–200° for 2 hrs. (118)) or by dilute acid (even in s.t. at 150° (118)); however, $\bar{C}$ with aq. in sunlight is claimed (123) to give formaldehyde (1:0145) + CO_2 + HCl (presumably by formn. and decompn. of OCH C(OH)$_3$), and $\bar{C}$ with aq. is claimed (124) to undergo slight formn. of dichloroacetic acid (3:6208) + HCl.

$\bar{C}$ with alc. KOH gives (125) $CHCl_3$ (3:5050) + ethyl formate (1:3000).

[Note that chloral deuterate, $CCl_3CH(OD)_2$ (from $\bar{C}$ + D_2O), with NaOD (17) or Ca-$(OD)_2$ (127) in D_2O gives deuteriochloroform, $CDCl_3$, b.p. 0.5° higher than ord. $CHCl_3$

(3:5050), m.p. −64.69 to −64.15°, D_4^{20} = 1.5004 (higher than 1.4888 for $CHCl_3$), n_D^{20} = 1.4450 (same as $CHCl_3$) (17).]

Behavior of C̄ with Ammonia, Hydroxylamine, Hydrazine, etc.

With NH_3. [C̄ with dry NH_3 gas (81) (48) in dry $CHCl_3$ (128) (129) or chloral hydrate (3:1270) with NH_3 in dry ether (129) gives a white solid, m.p. *72–74° (129), 62–64° (128)*, originally (81) (48) (128) regarded as chloralammonia $CCl_3.CH(OH).NH_2$ but later (on discovery of double the expected mol. wt. (129) cf. (130)) thought to have structure $CCl_3.CH(OH).NH.CH(NH_2).CCl_3.H_2O$. — The prod. with KCN in conc. aq. NH_4OH gives (93% yield (131)) dichloroacetamide, m.p. 98.5–99.0° (131).]

[Note that chloral hydrate (3:1270) with NH_4OAc at 100° gives (132) a prod., cryst. from alc., m.p. 97°, regarded as a dimeric form [Beil. XXIII-15] of chloralimide, $CCl_3{-}CH{=}NH$; this dimer is also accompanied (132) cf. (133) by two stereoisomeric trimers [Beil. XXVI-9–10] of chloralimide.]

With hydroxylamine. The behavior of C̄ with hydroxylamine differs according to the circumstances employed.

[C̄ as chloral hydrate (3:1270) with large excess $NH_2OH.HCl$ (4 moles) in a little aq. *(134) or with $NH_2OH.HCl$ (1 mole) in pres. of conc. aq. $CaCl_2$ (2 moles) at 50–60° (135)* gives trichloroacetaldoxime, m.p. 56° (135), 39–40° (134), b.p. 85° at 20 mm. (135).]

[C̄ as chloral hydrate (3:1270) with $NH_2OH.HCl$ (3 moles) in aq. Na_2CO_3/aq. NaOH as directed (136) (137) gives (yields: 50% (137), 40% (136) (138)) the alkali-stable form of chloro-oximino-acetaldehyde oxime ("chloroamphiglyoxime") [Beil. III-605, III_1-(216), III_2-(393)], ndls. of monohydrate from boilg. aq., m.p. 114° (136) (138) cf. (137); note that this prod. in dry ether with HCl gas (136) or with fumg. HCl (138) isomerizes to the acid-stable form ("chloroantiglyoxime") [Beil. III-606, III_1-(216), III_2-(393)], m.p. 161° (138), 161° dec. (136).]

[Note, however, that chloral hydrate (3:1270) (1 mole) with $NH_2OH.HCl$ (2 moles) powdered with dry Na_2CO_3 (1 mole), allowed to stand in a desiccator some hours, then dissolved in aq. and extracted with ether gives (139) an addition product, cryst. from ether, $CHCl_3$, or C_6H_6, m.p. 98°, regarded as chloralhydroxylamine, $CCl_3.CH(OH).NH.OH$.]

[For behavior of C̄ with $NH_2OH.HCl$ + aniline giving isatin see below under reaction of C̄ with primary aromatic amines.]

With Hydrazine

[C̄ as chloral hydrate (3:1270) with hydrazine hydrate in aq. (140), ether (141), or AcOH (142), or merely fused with hydrazine hydrochloride or sulfate (143), appears to give first the expected addition product, viz., chloralhydrazine, $CCl_3.CH(OH).NH.NH_2$, ndls. from alc., m.p. 100° (141), 85° dec. (140); note, however, that this structure is not certain and that the material readily changes to a compound $C_4H_2ON_2Cl_6$, m.p. 187° cf. (140) (141) (142) (143).]

Behavior of C̄ with Miscellaneous Inorganic Reactants

With various compounds of phosphorus. [C̄ with PCl_5 in acetone gives a product regarded (144) cf. (145) as $CCl_3.CH\Big\langle{O \atop O}\Big\rangle PCl_3$, b.p. 238–242°, accompanied by tetrachloroethylene (3:5460) and pentachloroethane (3:5880).]

[C̄ with PCl_3Br_2 is claimed (146) to give 1,1-dibromo-2,2,2-trichloroethane [Beil. I-93, I_1-(65)], b.p. 93–95° at 14–15 mm., $D_4^{19.5}$ = 2.295, $n_D^{25.7}$ = 1.52991 (146).]

[$\bar{C}$ with P_2S_5 in s.t. at 160–170° gives (147) a complicated reaction mixture from which only trichloroethylene (3:5170) has been identified.]

With various salts of inorganic acids (for KCN see further below).

With alkali bisulfites (or sulfites) [$\bar{C}$ or its hydrate (3:1270) with aq. alk. bisulfites (81) (149) reacts readily; for discussion of products see (81) (150) (151).]

With hydrogen peroxide. [$\bar{C}$ with H_2O_2 in ether (151), or $\bar{C}$ with $K_2S_2O_8 + H_2SO_4$ at ord. temp., gives (152) "dichloralperoxide hydrate," viz., $CCl_3.CH(OH)—O.O.CH(OH).CCl_3$, cryst. from C_6H_6 or $CHCl_3$, m.p. 122° dec.]

CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

BEHAVIOR OF $\bar{C}$ WITH HYDROCARBONS

With alkanes. [$\bar{C}$ with aliphatic hydrocarbons in presence of $AlCl_3$ reacts violently, but no definite products have been isolated (153).]

With aromatic hydrocarbons. $\bar{C}$ with aromatic hydrocarbons in presence of H_2SO_4 or other condensing agent (note that, when H_2SO_4 is present in large excess, chloral hydrate (3:1270) is frequently substituted for $\bar{C}$) reacts in either or both of two modes: $\bar{C}$ with 1 mole of hydrocarbon giving trichloromethyl-aryl-carbinols, $\bar{C}$ with 2 moles of hydrocarbon giving 1,1,1-trichloro-2,2-diarylethanes. Although reaction of $\bar{C}$ with hydrocarbons cannot here be summarized for all possible cases, yet the following examples will exemplify both modes of reaction.

[$\bar{C}$ with $C_6H_6 + AlCl_3$ (154) (156) or chloral hydrate (3:1270) with $C_6H_6 + AlCl_3$ (153) cf. (158) (162) or with C_6H_6 + conc. H_2SO_4 (155) gives trichloromethyl-phenyl-carbinol [Beil. VI-476, VI_1-(237)], m.p. 37° (155), b.p. 145° at 15 mm. (155) (corresp. acetate, m.p. 87.5° (155); corresp. benzoate, m.p. 97.5° (155); corresp. *p*-nitrobenzoate, m.p. 109° (156)) accompanied (155) by 1,1,1-trichloro-2,2-diphenylethane (3:1420), the latter also obtainable from $\bar{C} + C_6H_6$ with conc. H_2SO_4 (157) or with $AlCl_3$ in CS_2 (80% yield (162)).]

[$\bar{C}$ with toluene + $AlCl_3$ (154) or chloral hydrate (3:1270) (3 moles) with toluene (1 mole) + conc. H_2SO_4 (155) gives trichloromethyl-*p*-tolylcarbinol [Beil. VI-508, VI_1-(255)], m.p. 63–64° (154), 63° (155), 61.5–62.5° (159), 58–59° (160); b.p. 155° at 13.5 mm. (155), 154–156° at 13.5 mm. (154) (corresp. acetate, m.p. 107.5° (155), 105–106° (160); corresp. benzoate, m.p. 100.5° (155), 94–95° (160)). — On the other hand $\bar{C}$ with toluene (2 moles) in pres. of H_2SO_4 (161), or $AlCl_3$ (153) in CS_2 at 0° (162) gives (80% yield (162)) 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)ethane [Beil. V-619, V_1-(292), V_2-(522)], m.p. 89° (161) (162) (155), also obtained as by-product of the above carbinol (155); for study of loss of HCl with alc. KOH yielding 1,1-dichloro-2,2-di-(*p*-tolyl)ethylene [Beil. V-648, V_2-(559)], m.p. 92° (161), 85° (162) see (161) (162) (163).]

[For generally analogous behavior of $\bar{C}$ with other aromatic hydrocarbons such as *ter*-butylbenzene (405), *m*-xylene (153) (163), ethylbenzene (155), naphthalene (164), anthracene (164), or phenanthrene (164) in presence of condensing agents see indic. refs.]

BEHAVIOR OF $\bar{C}$ WITH ARYL HALIDES

With chlorobenzene. [That $\bar{C}$ with chlorobenzene (3:7903) (1 mole) + conc. H_2SO_4 gives the expected trichloromethyl-*p*-chlorophenyl-carbinol, b.p. 187–188° at 26 mm. (165) (corresp. acetate, m.p. 120–121° (165); corresp. benzoate, m.p. 128–129° (165)), has never been reported, this prod. having been obtd. only by condensation of *p*-chlorobenzaldehyde (3:0765) with $CHCl_3$ (3:5050) in pres. of KOH (23.5% yield (165)).

However, $\bar{C}$ or chloral hydrate with chlorobenzene (2 moles) + conc. H_2SO_4 gives the

extremely important 1,1,1-trichloro-2,2-*bis*-(*p*-chlorophenyl)ethane ("DDT") (3:3298) whose text should be consulted for further details.

With bromobenzene. [That C̄ with bromobenzene (1 mole) + conc. H_2SO_4 gives the expected trichloromethyl-*p*-bromophenyl-carbinol, b.p. 183–187° at 18 mm. (166) (corresp. acetate, m.p. 145–147° (166)), has never been reported, this product having been obtd. (29% yield (166)) only by reaction of C̄ with *p*-$Br.C_6H_4.MgCl$.]

[However, C̄ or chloral hydrate (3:1270) with bromobenzene (2 moles) + conc. H_2SO_4 + fumg. H_2SO_4 gives (167) (168) 1,1,1-trichloro-2,2-*bis*-(*p*-bromophenyl)ethane, m.p. 144° (167), 139–141° (168); note that this prod. with alc. KOH loses HCl, giving (82% yield (167) (168)) 1,1-dichloro-2,2-*bis*-(*p*-bromophenyl)ethylene, m.p. 123.5° (167), 119–120° (168).]

With iodobenzene. [The carbinol to be expected from C̄ with iodobenzene (1 mole) + conc. H_2SO_4 has not been reported.]

[However, C̄ with iodobenzene (2 moles) + conc. H_2SO_4 gives (155) 1,1,1-trichloro-2,2-*bis*-(*p*-iodophenyl)ethane, m.p. 172° (155).]

Behavior of C̄ with Organic Hydroxy Compounds

With Alcohols

General. Since C̄ is an aldehyde, it may be expected (at least with the assistance of a condensing agent such as dry HCl) to react with 1 mole of an alcohol to yield the corresponding hemiacetal, $CCl_3.CH(OH)R$, with 2 moles of an alcohol to give the corresponding acetal, $CCl_3.CH(OR)_2$, particularly since both these types of products are well known.

However, the special influence of the $-CCl_3$ group becomes apparent in this reaction and only the first type (hemiacetals) are usually obtained by direct condensation, the latter (acetals) being obtained indirectly. Moreover, members of the first group (hemiacetals) are formed with extreme ease (even in absence of condensing agents) so that, by analogy to the combination of chloral with water to give chloral hydrate (3:1270), they are generically designated as chloral alcoholates; e.g., chloral methylalcoholate, chloral ethylalcoholate, etc. Corresponding reaction of several molecules of chloral with multihydric alcohols can also occur as illustrated below.

The formation of these chloralalcoholates is profoundly influenced by conditions (especially the solvent (169)); furthermore, they readily dissociate into their original components on heating and, therefore, on heating in other alcohols (170) (171) or orthoformate esters of other alcohols (170) suffer reactions involving redistribution of the various alkyl radicals.

With monohydric alcohols. Although reaction of C̄ with all possible monohydric alcohols obviously cannot be included here, the following examples will serve to exemplify the reaction.

With methyl alcohol. [C̄ with MeOH (1:6120) (1 mole) gives (171) (172) (173) (174), trichloroacetaldehyde monomethylacetal (chloral methylalcoholate), hygroscopic ndls., m.p. abt. 50° (172), 38° (171), b.p. 116° (173), 106° (172), 98° (174) (corresp. carbamate, m.p. 121° (175)). — Note that trichloroacetaldehyde dimethylacetal, $CCl_3.CH(OCH_3)_2$ [Beil. I-621, I_1-(681)], b.p. 183.2° cor. (176), 68–69° at 10 mm. (177), is obtd. by indirect means; note incidentally that this acetal is isomeric with butyrchloral hydrate (3:1905) and with chloral ethylalcoholate (3:0860).]

With ethyl alcohol. [C̄ with EtOH (1:6130) gives trichloroacetaldehyde monoethylacetal (chloral ethylalcoholate) (3:0860), q.v. for details. For the corresp. acetal, viz., trichloroacetaldehyde diethylacetal, $CCl_3.CH(OC_2H_5)_2$, b.p. 204°, see its own text as 3:6317.

With n-propyl alcohol. [$\bar{C}$ with n-PrOH (1:6150) (178) (171) (170), or with NaO-n-Pr (179) or chloral hydrate (3:1270) with n-PrOH (1:6150) (170) gives (yields: 90% (178), 77–90% (170)) trichloroacetaldehyde n-propylhemiacetal (chloral n-propylalcoholate), liquid, b.p. 119–121° at 742.4 mm. (170), 120–122° (178), $D_4^{25.7}$ = 1.2996 (170), n_D^{25} = 1.4622. (Note that the corresp. trichloroacetaldehyde di-n-propylacetal is unreported.)]

With isopropyl alcohol. [$\bar{C}$ with iso-PrOH (1:6135) (178) (171) gives trichloroacetaldehyde isopropylhemiacetal (chloral isopropylalcoholate), m.p. 47° (178), 45° (171); b.p. 108° (178) (note that the corresp trichloroacetaldehyde di-isopropylacetal is unreported).]

With n-butyl alcohol. [$\bar{C}$ with n-BuOH (1:6180) gives (171) (179) (170) trichloroacetaldehyde n-butylhemiacetal (chloroal n-butylalcoholate) (3:0843), m.p. 49–50° (180), 49° (171) (170), b.p. 129–130° at 742 mm. (170) (note that corresp. trichloroacetaldehyde di-n-butylacetal is unreported).]

With isobutyl alcohol. [$\bar{C}$ with iso-BuOH (1:6165) gives (180) trichloroacetaldehyde isobutylhemiacetal (chloral isobutylalcoholate), liquid, b.p. 122° without decompn. (180); note that trichloroacetaldehyde di-isobutylacetal, b.p. 241.8° at 760 mm. (181), has been prepared indirectly).]

With sec-butyl alcohol. [$\bar{C}$ with butanol-2 (1:6155) gives (180) (171) trichloroacetaldehyde *sec*-butylhemiacetal (chloral *sec*-butylalcoholate), m.p. 12° (171), b.p. 120–121° (180), note that the corresp. trichloroacetaldehyde di-*sec*-butylacetal is unreported.]

With ter-butyl alcohol. [$\bar{C}$ with *ter*-butyl alc. (1:6140) gives (171) trichloroacetaldehyde *ter*-butylhemiacetal (chloral *ter*-butylalcoholate), m.p. 43° (171) (note that the corresp. trichloroacetaldehyde di-*ter*-butylacetal is unreported).]

With other monohydric alcohols. [For analogous formn. of hemiacetals from $\bar{C}$ with isoamyl alc. (1:6200) (180), with *ter*-AmOH (1:6160) (171), with allyl alc. (1:6145) (99), with n-octyl alc. (1:6255) (171), with benzyl alc. (1:6480) (171), with cinnamyl alc. (1:5920) (171), with methyl-neopentyl-carbinol (182), or with β,β,β-trichloro-*ter*-butyl alcohol ("Chloretone") (3:2662) (183) see indic. refs.]

With dihydric alcohols. *With ethylene glycol.* [$\bar{C}$ (1 mole) with ethylene glycol (1:6465) (1 mole) at 0° for 2 weeks gives (184) cf. (185) trichloroacetaldehyde (β-hydroxyethyl)-hemiacetal ("chloral ethyleneglycolate"), m.p. 50–51° (184), 42° (185); note that this product with conc. H_2SO_4 on stdg. or htg. loses 1 H_2O with ring closure to the cyclic acetal, 2-(trichloromethyl)-1,3-dioxolane, m.p. 40° (184). — However, $\bar{C}$ (2 moles) with ethylene glycol (1:6465) (1 mole) gives (186) cf. (185) ethylene glycol 1,2-*bis*-(β,β,β-trichloro-α-hydroxyethyl) ether, which on distn. at ord. press. also gives (186) the above 2-(trichloromethyl)-1,3-dioxolane, m.p. 42° (186).]

With polyhydric alcohols. *With glycerol.* [For behavior of $\bar{C}$ with glycerol (1:6540) see (186) (184).]

With erythritol. [For behavior of $\bar{C}$ with erythritol (1:5825) see (186).]

With various carbohydrates. $\bar{C}$ combines with various polyhydroxy compounds of the carbohydrate type to give products collectively designated as chloraloses. Such combinations can be effected with pentoses or hexoses, with various stereoisomers within any such group, and more than one molecule of chloral per mole of carbohydrate is sometimes involved. In the light of modern work these chloraloses are probably cyclic acetals. Although space cannot here be taken for an extensive record, the following comments will serve as starting points for further exploration.

The most important chloralose is that derived from d-glucose and often indexed as glucochloralose. Two forms of this compound are known, viz., α-glucochloralose and β-glucochloralose; for important studies of their structures see (187) (188). *For study of β-xylochloralose see* (189)

For important (but older) factual data on chloraloses see (190) (191) (192).

Behavior with Organic Acids

With Acids Containing No Other Functional Group

[For behavior of C̄ with AcOH in pres. of $AlCl_3$ see (153); with $Hg(OAc)_2$ + ethylene in alc. soln. giving a prod. possibly having the structure $CCl_3.CH(OC_2H_5)$ (OCH_2CH_2-HgOAc) see (215).]

[Note that C̄ is able to add to its carbonyl group a reactive H atom derived from certain acids [e.g., C̄ with malonic acid (1:0480) in AcOH at 100° for 40 hrs. (216) cf. (217), or in pyridine at 100° for 2 hrs. (67.5% yield (218)) cf. (219), or chloral hydrate (3:1270) + malonic acid (1:0480) + pyridine at 100° (220) gives (note loss of CO_2) γ,γ,γ-trichloro-β-hydroxy-*n*-butyric acid [Beil. III-310, III_1-(117), III_2-(221)], m.p. 118–119° (217) (218), 118.5° (216) (note hydrate, m.p. 52–54° (218)); note also that by further elimination of H_2O (e.g., with Ac_2O + NaOAc (217)) this prod. yields γ,γ,γ-trichlorocrotonic acid [Beil. II-418, II_1-(190), II_2-(397)], m.p. 113–114° (217).]

[Similarly, C̄ adds one of the α H atoms from succinic acid (1:0530): e.g., C̄ with disodium succinate + Ac_2O yields an intangible intermediate which suffers two types of further change, on one hand losing H_2O to give trichloromethylparaconic acid (β-carboxy-γ-trichloromethyl-γ-butyrolactone) [Beil. XVIII-372], and on the other suffering hydrolysis of its $-CCl_3$ group to give isocitric acid (α-hydroxypropane-α,β,γ-tricarboxylic acid) [Beil. III-555, III_2-(359)]; for details of execution of these reactions see (221).]

With α-Hydroxy Acids

Condensation of C̄ (or its hydrate) with acids containing an α-hydroxy group leads to the formation of products generically designated as "chloralides"; these are ether-esters comprising position-5 substitution products of the true parent 2-(trichloromethyl)-1,3-dioxolanone-4 (from α-hydroxyacetic acid) and are not to be confused with the specific compound "chloralide" (3:3510) obtd. from C̄ with H_2SO_4. With true chloralides above the initial parent, two geometrically isomeric forms are possible.

With α-hydroxyacetic acid. [C̄ with glycolic acid (1:0430) in s.t. at 120–130° for 2 days gives (224) 2-(trichloromethyl)-1,3-dioxolanone-4 ("glycolic acid chloralide") [Beil. XIX-103], m.p. 41–42°.]

(228), 70–71° (231), 59–60° (227); note that this disagreement of m.p.'s may be due to mixtures of possible *cis-trans* stereoisomers.]

With benzilic acid. [$\bar{C}$ with benzilic acid (1:0770) in s.t. at 160–165° for 5 hrs. gives (231) 2-(trichloromethyl)-5,5-diphenyl-1,3-dioxolanone-4 ("benzilic acid chloralide"), m.p. 70°. Note that an analogous prod. has been reported (232) from chloral hydrate (3:1270) with thiobenzilic acid, $(C_6H_5)_2C(SH)COOH$ in AcOH + HCl gas.]

With tartaric acid. [Since this acid is twice an α-hydroxy acid it reacts with 2 moles of $\bar{C}$ forming a dichloralide of compn. $C_8H_4O_6Cl_6$: e g., $\bar{C}$ with *d*-tartaric acid (1·0525) at 150° (224), or chloral hydrate (3:1270) with *d*-tartaric acid (1:0525) (227) (228) (229) (230) (231) or *d,l*-tartaric acid (1:0550) (227) (228) gives "tartaric acid dichloralide" [Beil. XIX-449], m.p. 213–215° (229); 164–166° (227), 161–162° (231), 161° (229), 160° (228), 159–161° (227); 128–130° (228), 122–124° (224), 116–118° (227). Note that this product should exist in three stereoisomeric forms (230), and the three groups of m.p.'s above given may represent this expectation]

With mucic acid. This acid combines with 3 moles of chloral hydrate to give a prod. commonly called a "trichloralide", note, however, that it is undoubtedly a dichloralide which has further condensed at its two free OH groups with a third molecule of chloral [e.g., chloral hydrate (3:1270) with mucic acid (1·0845) + H_2SO_4 gives (228) (229) a "trichloralide," m.p. 200–201° (228), 198° (229), 174–175° (229); doubtless these represent at least two stereoisomeric forms].

With Phenolic Acids (or Their Ethers)

In condensation of $\bar{C}$ (or its hydrate) with phenolic acids, the latter behave like carboxy-substituted phenols; two series of products result according to whether *one* or *two* moles of carboxy-phenol are involved per mole of chloral. To assist in recognizing this analogy, the several products are here named as substituted carbinols or ethanes just as was done above in the behavior of $\bar{C}$ with phenols (q.v.). Since the methyl ethers of these phenolic acids in general behave similarly, they are associated below with the corresponding phenolic acids.

With o-phenolic acids. *With o-hydroxybenzoic acid.* [Chloral hydrate (3:1270) with salicylic acid (1:0780) + conc. H_2SO_4 gives (233) cf. (234) some 1,1,1-trichloromethyl-(4-hydroxy-3-carboxyphenyl)-carbinol, m p. 180–182° (233), but main prod. is 1,1,1-trichloro-2,2-*bis*-(4-hydroxy-3-carboxyphenyl)ethane, m.p. 290–292° (corresp. diacetate, m.p. 207–209° (233)).]

With o-methoxybenzoic acid. [Chloral hydrate (3:1270) with *o*-methoxybenzoic acid (1:0685) + conc. H_2SO_4 gives (yields: 45% (234), 25% (235)) 1,1,1-trichloro-(4-methoxy-3-carboxyphenyl)-carbinol, m p. 224° (234), 216° (235), some sulfonation also occurring (235).]

With 2-hydroxy-3-methylbenzoic acid. [Chloral hydrate (3:1270) with *o*-cresotic acid [Beil. X-220, X_1-(96)] + conc. H_2SO_4 gives (236) 1,1,1-trichloro-2,2-*bis*-(4-hydroxy-3-methyl-5-carboxyphenyl)ethane, m.p. 283–285° (236): note that the *corresp. carbinol* to be expected from chloral hydrate + 1 mole *o*-cresotic acid is *unreported*.]

With 2-hydroxy-4-methylbenzoic acid. [Chloral hydrate (3:1270) with *m*-cresotic acid [Beil. X-233, X_1-(100)] is complex and disputed; for discussion see (236) (237) (238) (239). — For behavior of $\bar{C}$ with 2-methoxy-4-methylbenzoic acid see also (241).]

With 2-hydroxy-5-methylbenzoic acid. [Chloral hydrate (3:1270) with *p*-cresotic acid [Beil. X-227, X_1-(98)] + conc. H_2SO_4 gives (236) a prod. of compn. $C_{12}H_8O_4Cl_6$ (2,4-*bis*-(trichloromethyl)-6-methyl-1,3-benzdioxin-8-carboxylic acid), m.p. 285–286° dec., derived from 2 moles chloral hydrate + 1 mole *p*-cresotic acid.]

With 2-hydroxy-3-naphthoic acid. [For behavior of chloral hydrate (3:1270) with 2-hydroxy-3-naphthoic acid (1:0850) + conc. H_2SO_4 see (242).]

With *m*-phenolic acids (or their ethers). Condensation of $\bar{C}$ or its hydrate with *m*-phenolic acids leads generally to substituted phthalides.

With m-hydroxybenzoic acid. [Chloral hydrate (3:1270) with *m*-hydroxybenzoic acid (1:0825) + conc. H_2SO_4 gives (243) (244) 3-(trichloromethyl)-6-hydroxyphthalide [Beil. XVIII-20], m.p. 199–200° (244), 197–198° (243). — Note that chloral hydrate (3:1270) with ethyl *m*-methoxybenzoate (1:4131) + conc. H_2SO_4 gives (243) (245) 3-(trichloromethyl)-6-methoxyphthalide [Beil. XVIII-20], m.p. 135° (243) (245), which by alk. hydrol. of the —CCl_3 group gives (243) (245) 6-methoxyphthalide-3-carboxylic acid [Beil. XVIII-525], m.p. 170° (245), 169-170° (243).]

With 2-chloro-3-hydroxybenzoic acid. [Chloral hydrate (3:1270) with 2-chloro-3-hydroxybenzoic acid (3:4395) + conc. H_2SO_4 gives (246) 3-(trichloromethyl)-7-chloro-6-hydroxyphthalide, m.p. 195.5–196°.]

With 4-methyl-3-hydroxybenzoic acid. [Chloral hydrate (3:1270) with 4-methyl-3-hydroxybenzoic acid [Beil. X-237] + conc. H_2SO_4 gives (247) 3-(trichloromethyl)-5-methyl-6-hydroxyphthalide, m.p. 232° (247). — Similarly, chloral hydrate (3:1270) with 4-methyl-3-methoxybenzoic acid + conc. H_2SO_4 gives (247) 3-(trichloromethyl)-5-methyl-6-methoxyphthalide, m.p. 132° (247).]

With 3,4,5-trihydroxybenzoic acid. [Chloral hydrate (3:1270) with gallic acid (1:0875) + conc. H_2SO_4 gives (236) according to conditions three different products: with excess of gallic acid prod. is 3-(trichloromethyl)-4,5,6-trihydroxyphthalide, m.p. 210–212° (236), for further reactions of which see (236) (248); with excess chloral, however, the reaction gives two other materials (236). — Note that chloral hydrate (3:1270) with 3,4,5-trimethoxybenzoic acid (gallic acid trimethyl ether) [Beil. X-481, X_1-(240)] + conc. H_2SO_4 (249) (250) (251), or with methyl 3,4,5-trimethoxybenzoate (methyl gallate trimethyl ether) [Beil. X-484, X_1-(242)] (252), gives (56% yield (249)) 3-(trichloromethyl)-4,5,6-trimethoxyphthalide [Beil. $XVIII_1$-(389)], m.p. 76–77° (249), 71–72° (250), 70–71° (252) (note also that during condensation some demethylation may occur (253), avoided by (251)); this prod. by hydrolysis of the trichloromethyl group yields 4,5,6-trimethoxyphthalide-3-carboxylic acid [Beil. $XVIII_1$-(544)], m.p. 147–149° (249), 147–148° (250), 147° (251), 146–149° (254), 142–143° (252).]

With *p*-phenolic acids (or their ethers). *With p-hydroxybenzoic acid.* [Chloral hydrate (3:1270) (3 moles) with *p*-hydroxybenzoic acid (1:0840) (1 mole) + conc. H_2SO_4 at room temp. for 3 days condenses giving (31% yield on the acid (255)) 2,4-*bis*-(trichloromethyl)benzodioxin-1,3-carboxylic acid-6, m.p. 225.5–226.5° (255); for further related reactions of this prod. see (256); for further generally similar work in benzodioxin series see (257) (258); note that neither the substituted carbinol nor the substituted ethane corresp. to the behavior of *o*-hydroxybenzoic acid (see above) under similar conditions is reported.]

With p-methoxybenzoic acid. [Chloral hydrate (3:1270) with *p*-anisic acid (1:0805) + conc. H_2SO_4 reacts in a 1:1 ratio (note difference from 2:1 ratio in preceding paragraph) giving (259) cf. (235) trichloromethyl-(2-methoxy-5-carboxyphenyl)-carbinol, m.p. 198–199° (259); note that the earlier product (235) was impure.]

With 4-hydroxy-3,5-dimethoxybenzoic acid. [Chloral hydrate (3:1270) with syringic acid (1:0830) + conc. H_2SO_4 gives (86% yield (253)) 3-(trichloromethyl)-5-hydroxy-4,6-dimethoxyphthalide, m.p. 172–173° (253).]

With keto acids (see also below under behavior with esters of organic acids).

With levulinic acid. [$\bar{C}$ (1 mole) with β-acetopropionic acid (levulinic acid) (1:0405)

(312) (corresp. acetate, b.p. 156–157° at 685 mm.; corresp. benzoate m. (312)), but whether the material still unaccounted for represents (3:5775) from reduction of C̄ has not been reported.]

with n-BuMgBr in ether gives (34–36% yield (312)) the carbinol ,1-trichlorohexanol-2 [Beil. I_2-(438)], b.p. 108° at 673 mm., D_{20} = etate, b.p 157–158° at 684 mm.; corresp. benzoate, b.p. 182–183° whether the material still unaccounted for represents 2,2,2-trichloro- reduction of C̄ has never been reported.]

X *cpds* [C̄ with n-AmMgBr (313) or with n-HexMgBr (313) in ectively 50–61% and 56–69%) the reduction product, 2,2,2-tri-); the corresponding carbinols to be expected by addition are

compounds. *With C_6H_5MgX.* [C̄ with C_6H_5MgBr in ether)) (315) the expected trichloromethyl-phenyl-carbinol [Beil. 37° (155), b.p 145° at 15 mm. (155) (corresp. acetate, m p. 87.5° m p. 97.5° (155); corresp. p-nitrobenzoate, m.p. 109° (156)).]

npounds. *With $C_6H_5CH_2MgX$ cpds.* [C̄ with $C_6H_5CH_2MgCl$ IgBr (166) gives both addition (309) (310) (166) and reduction ormer trichloromethyl-benzyl-carbinol, b p. 158–160° at 18 mm. p. 110–111° (166), 109–110° (309)), together with a very small hloroethanol-1 (3:5775).]

ds. [C̄ with cyclohexyl MgBr (314) (316) in ether is claimed trichloromethyl-cyclohexyl-carbinol, b p. 119–121° at 15 mm., 0 (*corresp. acetate, b p. 173° at 680 mm., corresp. benzoate,* nd also (42% yield (314)) 2,2,2-trichloroethanol-1 (3:5775).]

[For behavior of C̄ with the RMgX cpds. from β-phenylethyl omide, and δ-phenylbutyl bromide where the reaction appears see (317).]

EHAVIOR WITH HCN (OR ITS SALTS)

with strong aq. HCN refluxed several days (318) or chloral 0–12% HCN (319) (320) or with aq. 15% HCN in s.t. at 100° s (71% yield (321)) β,β,β-trichloro-α-hydroxypropionitrile = al cyanohydrin [Beil. III-288, III_1-(111), III_2-(210)], m.p. orresp. benzoate, m.p. 40–41° (323)); this prod. upon partial gives (324) trichlorolactamide [Beil. III-288, III_1-(111),), or on complete hydrolysis with conc. HCl (321) (318) (320) l. III-286, III_1-(111), III_2-(210)], very sol. aq., but cryst. 21).]

ith MeOH/KCN gives within 1 min. (84% yield (131)) 5); C̄ with EtOH/KCN similarly gives (88% yield (131))); C̄ with n-propyl alc./KCN similarly gives (70% yield te (3:6000); for extensive discussion of this reaction see

f chloral hydrate (3:1270) with KCN in C_6H_6 see (326): 70) with NaCN + $CaCO_3$ as directed (328) is an important d) of dichloroacetic acid (3:6208) q.v.: note also that H_4OH + KCN in ether as directed (329) gives (65–78% nder the acid (3:6208).]

Behavior with Diazomethane

[$\bar{C}$ (309) (330) (331) or chloral hydrate (3:1270) (332) gives (yields: 64% (330), 48% (309), 47.5% (332)) 3,3,3-trichloro-1,2-epoxypropane (3:5760) q.v.]

Behavior with Amines

With primary aromatic amines. *With aniline.* [$\bar{C}$ with aniline (333) (334), or chloral hydrate (3:1270) with aniline in aq. (334), gives 1,1,1-trichloro-2,2-dianilinoethane (β,β,β-trichloroethylidene)di-aniline [Beil. XII-187, XII_1-(168)], pr. from ether/alc., m.p. 107–108° (335), 107.5° (334), 100–101° (333). — Note that the addition product to be expected from 1 mole $\bar{C}$ with 1 mole aniline has not itself been isolated (except as a molecular compound with chloral hydrate (336)) since it appears to react immediately with a second mole of aniline to give the above-indicated prod.]

With aniline + hydroxylamine. [Chloral hydrate (3:1270) (1 mole) with aniline (1 mole) + $NH_2OH.HCl$ (3 moles) + HCl + Na_2SO_4 in aq. soln. as directed gives (80–91% yield (337)) cf. (338) (339) isonitrosoacetanilide [Beil. XII_1-(275)], m.p. 175° dec. (337) (338) (339). — Note that this product with conc. H_2SO_4 (337) (340) gives (71–78% yield (337)) indigo; for extension of the method to use of other amines (and ultimately substituted indigos) see (338) (341) (345).]

With other primary aromatic amines. The condensation of $\bar{C}$ or of chloral hydrate (3:1270) with many other primary aromatic amines and diamines has been studied but cannot be detailed here [for extensive review and discussion see (336) (334) (335) (342) (343) (344) (403)].

With secondary aromatic amines. *With N-alkylanilines.* [Chloral hydrate (3:1270) with *N*-methylaniline on warming gives (346) trichloromethyl-(*p*-methylaminophenyl)-carbinol [Beil. XIII-628], m.p. 112° dec.; similarly, chloral hydrate (3:1270) with *N*-ethylaniline on warming gives (346) trichloromethyl-(*p*-ethylaminophenyl)-carbinol [Beil. XIII-628], m.p. 98°.]

With N-alkyl-o-toluidines. [Chloral hydrate (3:1270) with *N*-methyl-*o*-toluidine + $ZnCl_2$ gives (347) trichloromethyl-(4-methylamino-3-methylphenyl)-carbinol, m.p. 104–105°; similarly, chloral hydrate (3:1270) with *N*-ethyl-*o*-toluidine + $ZnCl_2$ gives (349) trichloromethyl-(4-ethylamino-3-methylphenyl)-carbinol, m.p. 107° (for studies of nitration (348) and bromination (349) of these two products see indic. refs.).]

With tertiary aromatic amines. *With N,N-dialkylanilines.* [$\bar{C}$ with *N*,*N*-dimethylaniline in phenol at room temp. (350) or chloral hydrate with *N*,*N*-dimethylaniline + $ZnCl_2$ on stdg. (351) (352) gives trichloromethyl-(*p*-dimethylaminophenyl)-carbinol [Beil. XIII-628], m.p. 111° dec. (352) (corresp. carbinyl acetate, m.p. 84–85° (352)) (for study of nitration of this prod. see (348)).]

Behavior with Arylhydrazines

With phenylhydrazine. [$\bar{C}$ with phenylhydrazine or chloral hydrate (3:1270) with aq. phenylhydrazine salts reacts (353) vigorously, but the products formed have not been unambiguously characterized (see also below).]

With *p*-nitrophenylhydrazine. [Chloral hydrate (3:1270) (large excess) with *p*-nitrophenylhydrazine in AcOH at 100° for 10 min. undergoes a series of reactions resulting (354) in a chlorine-free prod., m.p. 228°, regarded (354) as 1-(*p*-nitrophenyl)-3,5-dihydroxypyrazolone-4-(*p*-nitrophenylhydrazone).]

With 2,4-dinitrophenylhydrazine. [Chloral hydrate (3:1270) with 2,4-dinitrophenylhydrazine gives according to conditions either or both (355) glyoxylic acid *p*-nitrophenyl-

hydrazone, dihydrate from aq., m.p. 191° (355); anhydrous, m.p. 194–195° (355), 190° (356), or chloroglyoxal *bis*-(2,4-dinitrophenylhydrazone), m.p. 278° (355).]

With various halogenated hydrazines. Owing to the violence with which the product initially formed decomposes, the behavior of Č with phenylhydrazine (see also above) has been little studied. With halogenated phenylhydrazines the decomposition is more moderate and has been extensively examined. The nature of the products has been found to depend mainly upon the solvent medium: thus in alcohols the principal product is the corresponding substituted phenylhydrazone of the appropriate alkyl glyoxylate; in water or AcOH, however, loss of both H_2O and HCl occurs leading to formation of the corresponding α,α-dichloro-β-arylazoethylenes.

[Chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine in ethyl alc. at 60° gives (100% yield (357)) ethyl glyoxylate 2,4-dichlorophenylhydrazone, yellow pr., m.p. 121.5°, note that other alcs. (357) give corresp. esters. — However, chloral hydrate (1 mole) (3:1270) with 2,4-dichlorophenylhydrazine (1 mole) in AcOH at 80° (or in presence of NaOAc at 60°) gives (357) α,α-dichloro-β-(2,4-dichlorobenzeneazo)ethylene, red pr. from alc., m.p. 84.5°.]

[For completely analogous behavior of chloral hydrate (3:1270) with other halogenated phenylhydrazines, such as 2,5-dichlorophenylhydrazine (358), 2,4,5-trichlorophenylhydrazine (358), 2,4,6-trichlorophenylhydrazine (359), 2,4,6-tribromophenylhydrazine (359), 3-bromo-4-methylphenylhydrazine (360), or 3,5-dibromo-4-methylphenylhydrazine (360), see indic. refs. — Note that a generally analogous behavior toward halogenated arylhydrazines is shown by butyrchloral (3:5910) q.v. and by tribromoacetaldehyde (bromal).]

Behavior with Amides

Č with compounds of the amide type readily undergoes an addition reaction leading to products of the general form CCl_3 CH(OH).NH.CO.R.

With Aliphatic Monamides

With formamide. [Č (1 mole) with formamide (1 mole) on stdg. gives (361) (362) an addition prod., chloralformamide, CCl_3 CH(OH).NH.CHO [Beil. II-27, II_1-(21), II_2-(37)], m.p. 124–126° (363), 118° (362), 115–116° (361); note that this product has in the literature often been confused with the isomeric β,β,β-trichloroethyl carbamate, CCl_3.-CH_2O.CO.NH_2 ("Voluntal") [see also under β,β,β-trichloroethyl alcohol (3:5775)] Note also that chloralformamide with aq. NaOH + Ac_2O (362) or with aq. NaOH + BzCl (364) cf. (362) undergoes bimolecular condensation with loss of H_2O giving anhydrochloralformamide [CCl_3.CH(NH.CHO)$]_2$O, m.p. 194.5–195° (362), 193° (364).]

With acetamide. [Č (1 mole) with acetamide (1 mole) (72) (172), or chloral hydrate (3:1270) (1 mole) with acetamide (1 mole), or chloralammonia with AcCl or Ac_2O (128) gives chloralacetamide [Beil. II-179, II_1-(81)], m.p. 158–159° (362), 158° (172), 156°–157° (72), 156° (128); this prod. with aq. NaOH + Ac_2O undergoes bimolecular loss of aq. yielding (362) cf (369) anhydrochloralacetamide, [CCl_3 CH(NH.CO.CH_3)$]_2$O, m.p. 212–213° (362), 207° (364). — For study of reduction of chloralacetamide see (365) (366).]

With higher monoamides. [For analogous condensation of Č with propionamide, isobutyramide, *n*-valeramide, *n*-caproamide, *n*-caprylamide, and phenylacetamide together with study of reduction of the several products see (367) cf. (369).]

With Aromatic Monoamides

With benzamide. [Č (1 mole) with benzamide (1 mole) (172) (362) cf. (369), or chloral hydrate (3:1270) with benzonitrile + dry HCl (368) gives chloralbenzamide [Beil. IX-

209, IX_1-(101)], m.p. 150–151° (72), 150° (362), 146° (172) (368); this product with aq NaOH + BzCl or Ac_2O gives (362) by dehydrative bimolecular condensation anhydrochloralbenzamide, known (362) in two forms, higher-melting form, m.p. 199–200°, and lower-melting form, m.p. 137–138°. — For study of reduction of chloralbenzamide see (366) cf. (369).]

With toluamides. [For condensation of $\bar{C}$ with *o*-, *m*-, and *p*-toluamides see (370); for the behavior of the products with PCl_5 see (371).]

With salicylamide. [$\bar{C}$ with salicylamide on warming directly (372) or in $CHCl_3$ (373) gives chloralsalicylamide, sintering at 117° and melting about 10° higher (372); for the corresp. anhydro compound (cf. above), m.p. 174–175°, see (369); for studies of chloralsalicylamide on chlorination (374), bromination (375), or nitration (375) see indic. refs.]

With amides of various substituted salicylic acids. [For behavior of $\bar{C}$ with the amides of 3-chlorosalicylic acid (3:4745), 5-chlorosalicylic acid (3:4705), and 3,5-dichlorosalicylic acid (3:4935) see (374) (376) (377); for behavior of $\bar{C}$ with amides of various nitrosalicylic acids (378) or various aminosalicylic acids (379) see indic. refs.]

With *o*-aminobenzamide (anthranilamide). [For behavior of $\bar{C}$ with anthranilamide and its relatives see (380).]

With Amides of Dibasic Acids

Note that two series of products are formed.

With urea. [Chloral hydrate (3:1270) (1 mole) with urea (2 moles) in aq. soln. on stdg. 3 days at room temp. gives (66% yield (381)) (382) cf. (172) chloralurea, *N*-(β,β,β-trichloro-α-hydroxyethyl)urea [Beil. III-59, III_1-(27)], cryst. from $MeOH/C_6H_6$ (381) or $EtOH/C_6H_6$ 1:3 (382), m.p. 150° dec. (381) (382). — However, chloral hydrate (3:1270) (2 moles) with urea (1 mole) in aq. HCl at room temp. for 3 days gives (71% yield (381)) (382) cf. (383) dichloralurea [Beil. III-60, III_1-(27), III_2-(49)], cryst. from aq. alc., m.p. 196° (381), 194° dec. (382), 190° (172).]

With thiourea. [For behavior of $\bar{C}$ with thiourea see (383).]

With various substituted ureas. *With monosubstituted ureas.* [Chloral hydrate (3:1270) (2 moles) with *N*-methylurea (1 mole) in aq. soln. at room temp. gives (384) *N*-methyl-*N'*-(β,β,β-trichloro-α-hydroxyethyl) urea, m.p. 140° dec. (384). — Chloral hydrate (3:1270) with *N*-ethylurea behaves in analogous fashion (384). — Chloral hydrate (3:1270) (2½ moles) with *N*-phenylurea in aq. HCl gives (84% yield (382)) *N*-phenyl-*N'*-(β,β,β-trichloro-α-hydroxyethyl)urea, m.p. 142° dec. (382). — For corresp. behavior of chloral hydrate (3:1270) with *N*-*o*-tolylurea, *N*-*p*-tolylurea, *N*-*m*-nitrophenylurea, and *N*-*p*-nitrophenylurea see (385).]

With disubstituted ureas. [Chloral hydrate (3:1270) with *N,N*-dimethylurea gives (384) cf. (386) *N,N*-dimethyl-*N'*-(β,β,β-trichloro-α-hydroxyethyl)urea, cryst. from aq as monohydrate, m.p. 74° dec. (384) (386), which becomes anhydrous on stdg., cryst. from alc., m.p. 157° dec. (384), 156° (386). — For analogous behavior of $\bar{C}$ with *N,N*-diethylurea giving prod., m.p. 146° dec. (384), 142° (386), see indic. refs. — $\bar{C}$ with *N,N*-diphenylurea gives analogous prod., m.p. 170° dec. (384).]

With amides of other dibasic acids. [For generally analogous behavior of $\bar{C}$ with oxamide (384), malonamide (384) (369), succinamide (369), and their relatives see indic. refs.]

With Urethanes

With ethyl carbamate. [$\bar{C}$ with ethyl carbamate ("urethane") in conc. HCl gives (387) (388) ethyl *N*-(β,β,β-trichloro-α-hydroxyethyl)carbamate ("chloralurethane") [Beil. III-24, III_1-(12), III_2-(22)], m.p. 103° (362) (388). — This product on htg. alone or

in aq. at 100° regenerates (388) chloral and ethyl carbamate. — With AcCl under reflux it gives (80% yield (387)) the corresp. acetate, m.p. 47–49°, b.p. 165° at 15 mm. (387). — With aq. NaOH + Ac_2O (362) (387) or with aq. KOH + BzCl (364) chloralurethane undergoes dehydrative bimolecular condensation yielding anhydro-chloralurethane [Beil. III_1-12], which exists in both high-melting (161–162°) and low-melting (149–150°) forms (362).]

With other alkyl carbamates. [For generally analogous behavior of $\bar{C}$ with methyl carbamate (362), *n*-propyl carbamate (389), isobutyl carbamate (389), isoamyl carbamate (362), and menthyl carbamate (362) see indic. refs.]

Ⓟ Preliminary tests for $\bar{C}$: Owing to the length of the text of this compound, a brief summary of the tests most significant as preliminary indications is given here; for details refer back as indicated and also see chloral hydrate (3:1270).

$\bar{C}$ reduces $NH_3/AgNO_3$ and Fehling's soln. but only on warming (see above under oxidn of $\bar{C}$). — $\bar{C}$ gives fuchsin-aldehyde test with Schiff's reagent (but chloral hydrate (3 1270) does not). — $\bar{C}$ with conc. H_2SO_4 readily polymerizes (see above under polymerization of $\bar{C}$). — $\bar{C}$ with aq. or alc. alkali on warming undergoes hydrolytic cleavage to $CHCl_3$ (3·5050) + alkali formate (see above under behavior of $\bar{C}$ with alkalies); therefore, $\bar{C}$ with alc. alkali + aniline gives characteristic odor of phenyl isocyanide.

—— **Trichloroacetaldioxime:** m.p. 56° (135). [See above under behavior of $\bar{C}$ with hydroxylamine.]

—— **Trichloroacetaldehyde phenylhydrazone:** unreported. [See above under behavior of $\bar{C}$ with arylhydrazines.]

—— **Trichloroacetaldehyde *p*-nitrophenylhydrazone:** unreported. [See above under behavior of $\bar{C}$ with arylhydrazines]

—— **Trichloroacetaldehyde 2,4-dinitrophenylhydrazone:** a prod. of m.p. 131° has been claimed (390) but could not be confirmed (391). [See also above under behavior of $\bar{C}$ with arylhydrazines.]

—— **Trichloroacetaldehyde semicarbazone:** unreported. [Note that chloral hydrate (3:1270) with semicarbazide in aq. (392) (394) cf. (393) or chloral ethylalcoholate (3:0860) with semicarbazide in alc. (392) gives an addn. prod., m p. 90°, which on boilg. with aq. yields (392) glyoxylic acid semicarbazone [Beil. III-600, III_1-(209) III_2-(389)], m.p. 235–236° (392), 235–238° (393), 207° (395), 206–208° dec. (396), 202–203° (397), 202° dec. (394) (note that these results may represent two stereoisomeric forms (397)).]

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(391) Allen, Richmond, *J. Org. Chem.* **2**, 225 (1937). (392) Kling, *Bull. soc. chim.* (4) **5**, 412–414 (1909); *Compt. rend.* **148**, 569 (1909). (393) Knöpfer, *Monatsh.* **32**, 768–771 (1911). (394) Darapsky, Prabhakar, *Ber.* **45**, 2624–2625 (1912). (395) Müller, *Ber.* **47**, 3021 (1915). (396) Sah, Kao, Chang, *J. Chinese Chem. Soc.* **2**, 236 (1934). (397) Busch, Achterfeldt, Seufert, *J. prakt. Chem.* (2) **92**, 24 (1915). (398) Koenigs, *Ber.* **25**, 794–797 (1892). (399) Wislicenus, Kircheisen, Sattler, *Ber.* **26**, 908–915 (1893). (400) Sen, Barat, *J. Indian Chem. Soc.* **2**, 403–414 (1926).

(401) Uschakoff, *J. Russ. Phys.-Chem. Soc.* **29**, 113–116 (1897); *Cent.* **1897**, I 1019. (402) Koenigs, Wagstaffe, *Ber.* **26**, 554–556 (1893). (403) Sumerford, Dalton, *J. Org. Chem.* **9**, 81–84 (1944). (404) Frolich, Wiezevich (to Standard Oil Dev. Co.), U.S. 2,042,303, May 26, 1936; *Cent.* **1936**, II 3193; *C.A.* **30**, 4871 (1936); Ger. 629,897, May 26, 1936; *Cent.* **1936**, II 2448; *C.A.* **30**, 6006 (1936). (405) Cristol, Hayes, Haller, *J. Am. Chem. Soc.* **68**, 913–914 (1946).

3:5220 2,3-DICHLOROBUTADIENE-1,3 $C_4H_4Cl_2$ **Beil. S.N. 12**

$$\begin{array}{c} \quad\ Cl\ \ Cl \\ \quad\ \ |\ \ \ \ | \\ H_2C{=}C{-}C{=}CH_2 \end{array}$$

B.P. 98° at 760 mm. (1) (2)
41–43° at 85 mm. (1)
40–43° at 85 mm. (3)

$D_4^{20} = 1.1829$ (1)

$n_D^{20} = 1.4890$ (1)

[For prepn. of C̄ (86% yield (1)) from 1,2,3-trichlorobutene-3 (2,3,4-trichlorobutene-1) (3:9064) with excess MeOH/KOH at 10–15° see (1) (2); for formn. (together with other products) from 1,2,3,4-tetrachlorobutane (3:1760) with MeOH/KOH at 10–18° see (1) (2); from chloroprene (3:7080) by addn. of ICl followed by treatment with alc. KOH (3).]

C̄ polymerizes completely within 24 hrs. at room temp., in about 40 min. at 85–90°; this is about 10 times as fast as chloroprene (3:7080) and 7000 times as fast as isoprene (1:8020). The polymer is a white opaque tough hard mass, non-plastic and lacking extensibility. It is insol. in and separates from liquid C̄ but is partly soluble in $CHCl_3$ (1). The polymerization is inhibited by hydroquinone and accelerated by benzoyl peroxide (2).

C̄ does *not* (1) react with maleic anhydride (1:0625) or with 1,4-naphthoquinone (1:9040).

3:5220 (1) Carothers, Berchet, *J. Am. Chem. Soc.* **55**, 2004–2008 (1933). (2) Carothers, Berchet, U.S. 1,965,319, July 3, 1934; *Cent.* **1935**, I 3724; *C.A.* **28**, 5716 (1934). (3) Petrov, *J. Gen. Chem. (U.S.S.R.)* **13**, 155–158 (1943); *C.A.* **38**, 1466–1467 (1944).

3:5225 METHOXYACETYL CHLORIDE

$CH_3OCH_2—C=O$

Cl

im.
hem.
(30)
-1460
ler. 70,

B.P. 99° (1) D_4^{20} = 1.1871
50-51° at 69 mm. (2)

[For prepn. of Č from methoxyacetic acid (1:1065) with SOCl₂
(2)) see indic. refs. (note that best yield is obtd. with
since cleavage of the methoxy group is thus minimized)
[Beil. III_1-(92)] with $COCl_2$ (3:5000) at 160° under pressure
see (3); from chloromethyl methyl ether (3:7085)
with CO at 25-50° and 275-625 pounds press. for

Beil. I - 582
I_1-(305)
I_2-(646)

[Č with alcs. + pyridine in $CHCl_3$ soln. gives
benzyl alc. (1:6480), with β-phenylethyl alc.
see (1); with menthol (1:5940) see (5); for
(1:6480), cyclohexanol (1:6415), or ethylene
(2).]

n_D^{21} = 1.435 (2)

Č on hydrolysis yields methoxyacetic acid
derivs. corresp. to Č see methoxyacetic acid

hydrolysis to formaldehyde
(1 0080) (95% yield (6)), or
see (6) (7); from paraformalde-
see (8); for prepn. from dimethyl
by addn. to olefins see (11).]

3:5225 (1) Rothstein, *Bull. soc. chim.*
(3) Stellmann, French 785,075, Aug. 1,
U.S. 2,084,284, June 15, 1937; *Cent.*
J. Chem. Soc. 127, 2101 (1925).

3:5230 1,2,3-TRICHLORO-2-
BUTANE

het, *Ann. chim.* (7) 10, 297 (1897). (3)
(4) Litterscheid, *Ann* 330, 116 (1903).
2 3973 (1941)
Chem Ind
nts (to du Pc
of Booth (to
Cent 1937, I 3529.
17, 1935, Brit 423,520, *C.A.* 30, 1067 (1936); *C.A.*

PANE $CH_3CH_2CCl_3$ $C_3H_5Cl_3$ Beil. S.N. 10

D_4^{20} = 1.287 (1)

(2)

dichloropropene-1 (3:5120) + HCl + $AlCl_3$ at 5-10° see (1) (2)

in Beil. 1-106 as Č is erroneous (1) (3).]

Case (to d
du Pont), U.S. 2. (2)
41, 1101 (1932) Arkel,

[For prepn. of $\bar{C}$ from chloroacetic acid (3:1370) with PCl_3 (5) (40), or in HCl atm. under press. at 150° (6), or with $ZnCl_2$ (67% yield (7)) see indic. refs.; with P_2O_5 + HCl gas at 200° see (8); with $SOCl_2$ (yields: 95% (9), 55% (10), 50% (7)) (11) see indic. refs.; with benzoyl chloride (3:6240) (yield 71–76%) see (12); with oxalyl dichloride (3:5060) (80% yield) see (3); with phosgene (3:5000) over activated carbon at 200° see (13); with benzotrichloride (3:6540) + $ZnCl_2$ at 80–90° (80% yield) see (14); with Cl_2 + S_2Cl_2 (95% yield (15)) or Cl_2 + lower chlorides of sulfur + $FeCl_3$, $SnCl_4$, etc., at 50–60° (82% yield (16)) see indic. refs.]

[For prepn. of $\bar{C}$ from chloroacetic acid anhydride (3:0730) with oxalyl dichloride (3:5060) see (3); from ketene with NOCl see (17); from α,β-dichlorovinyl ethyl ether (3:5540) + HCl gas see (18); from α,β-dichloroethylene + O_2 in pres. of Br_2 or conc. H_2SO_4 see (19); from acetyl chloride (3:7065) with Cl_2 in sunlight (20) or in CCl_4 in u.v. light (21) or in pres. of I_2 (22) see indic. refs.; from α-chloroethyl chloroacetate on htg. with 0.02% $ZnCl_2$ see (23); from 2-(chloroacetoxy)hexene-1 with HCl gas see (24), from CH_2Cl_2 (3:5020) + $AlCl_3$ + CO gas at 200° and 900 atm. see (41).]

$\bar{C}$ on htg. with Na_2CO_3 (25) or with KNO_3 (81% yield (26)) gives chloroacetic acid anhydride (3:0730) q.v., m.p. 46°. — $\bar{C}$ treated at −5° with HI gas gives (68% yield (27)) chloroacetyl iodide, b.p. 36.5° at 4 mm. (27). [For behavior of $\bar{C}$ with HBr gas see (40).]

$\bar{C}$ with MeOH yields (28) methyl chloroacetate (3:5585), b.p. 131°; $\bar{C}$ with EtOH (29) or with triethyl orthoformate (1:3241) at 100–110° (90% yield (30)) gives ethyl chloroacetate (3:5700), b.p. 144°.

[$\bar{C}$ with ethylene + $AlCl_3$ gives (small yield (31)) 1,4-dichlorobutanone-2, b.p. 63–65° at 3 mm. (31). — $\bar{C}$ with C_6H_6 + $AlCl_3$ gives (32) ω-chloroacetophenone (phenacyl chloride) (3:1212); $\bar{C}$ with m-dichlorobenzene (3:5960) + $AlCl_3$ gives (33) 2,4-dichlorophenacyl chloride [Beil. VII-283], m.p. 57° (33); $\bar{C}$ with biphenyl + $AlCl_3$ gives (77% yield (34)) p-phenylphenacyl chloride (3:3934), m.p. 122–123° (34); $\bar{C}$ with naphthalene + $AlCl_3$ in CS_2 gives (35) cf. (36) chloromethyl β-naphthyl ketone.]

[$\bar{C}$ with large excess (4 moles) MeMgBr or MeMgI gives (48–51% yield (37)) (38) 2-methylbutanol-3 (1:6170); $\bar{C}$ with large excess C_6H_5MgBr in ether gives (31% yield (39)) 1,2,2-triphenylethanol-1 [Beil. VI-721], m.p. 87.5–88.5° (39); note that the isomeric 1,1,2-triphenylethanol-1 [Beil. VI_1-(354)] has almost same m.p., viz., 89°.]

$\bar{C}$ hydrolyzes with aq. yielding chloroacetic acid (3:1370) q.v. — For the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{C}$ see chloroacetic acid (3:1370).

3:5235 (1) Martin, Partington, *J. Chem. Soc.* **1936**, 162. (2) Cheng, *Z. physik. Chem.* **B-26**, 295 (1934). (3) Adams, Ulich, *J. Am. Chem. Soc.* **42**, 604, 606 (1920). (4) Vanderstichele, *J. Chem. Soc.* **123**, 1228 (1923). (5) de Wilde, *Ann.* **130**, 372–373 (1864). (6) Scheuble, Ger. 251,806, Oct. 8, 1912; *Cent.* **1912**, II 1503–1504. (7) Clark, Bell, *Trans. Roy. Soc. Canada* (3) **27**, III 97–103 (1933). (8) Frankland, Patterson, *J. Chem. Soc.* **73**, 190 (1898). (9) Barnett, *Chem. News* **122**, 220–221 (1921); *Cent.* **1921**, III 463. (10) McMaster, Ahmann, *J. Am. Chem. Soc.* **50**, 146 (1928).

(11) Böeseken, *Rec. trav. chim.* **32**, 5 (1913). (12) Brown, *J. Am. Chem. Soc.* **60**, 1325–1328 (1938). (13) Hochstetter, Ger. 283,896, April 27, 1915; *Cent.* **1915**, I 1190. (14) Rabcewicz-Zubkowski, *Roczniki Chem.* **9**, 526–527 (1929); *Cent.* **1929**, II 2767; *C.A.* **24**, 61 (1930). (15) Read, *J. Am. Chem. Soc.* **44**, 1751 Note (1922). (16) Britton (to Dow Chem. Co.), U.S. 1,805,162, May 12, 1931; *Cent.* **1931**, II 631; *C.A.* **25**, 3670 (1931). (17) Deakin, Wilsmore, *J. Chem. Soc.* **97**, 1977 (1910). (18) Consortium für Elektrochem. Ind., Ger. 222,194, May 19, 1910; *Cent.* **1910**, I 1999. (19) Consortium für Elektrochem. Ind., Ger. 340,872, Sept. 19, 1921; *Cent.* **1921**, IV 1101. (20) Wurtz, *Ann. chim.* (3) **49**, 60 (1857).

(21) Benrath, Hertel, *Z. wiss. Phot.* **23**, 35 (1924). (22) Jazukowitsch, *Zeit. für Chemie* **1868**, 234. (23) Soc. Usines C
1611. (24) Slanina, He
211–212 (1905). (26) D

Soc. 55, 375 (1933). (28) Meyer, *Ber.* 8, 1152–1158 (1875). (29) Willm, *Ann.* 102, 109–111 ...
(32) Friedel, Crafts, *Ann. chim.* ...
(34) Silver, Lowy, *J. Am. Chem.* ...
...hem. *Ind.* 44, 494-T (1925). (36) ...
J. Am. Chem. Soc. 63, 1459–1460 (1941). (38) Henry, *Compt. rend.* 145, 24 (1907). (39) Boyle, McKenzie, Mitchell, *Ber.* 70, 2159 (1937). (40) Aschan, *Ber.* 46, 2168 (1913).
(41) Theobald (to du Pont Co.) U.S. 2,378,048, June 12, 1945; *C.A.* 39, 4085 (1945).

3:5245 *sym.*-DICHLORODIMETHYL ETHER $C_2H_4OCl_2$ Beil. I - 582

(*bis*-(Chloromethyl) ether) $ClCH_2.O.CH_2Cl$ I_1-(305) I_2-(646)

B.P. 105° (1) (2) (8)	$D_{20}^{20} = 1.315$ (1)	$n_D^{21} = 1.435$ (2)
104–106° (3)	$D_4^{15} = 1.328$ (2)	
103–106° (4)		

Liq. fumg. in moist air.

$\bar{C}$ dis. slowly in cold and rapidly in warm aq. owing to hydrolysis to formaldehyde (1:0145) + HCl. [For quant. study see (5).]

[For prepn. from formalin (1:0145), paraformaldehyde (1:0080) (95% yield (6)), or hexamethylenetetramine + chlorosulfonic ac. + conc. H_2SO_4 see (6) (7); from paraformaldehyde (1:0080) + conc. H_2SO_4 + HCl gas (85% yield (8)) see (8); for prepn. from dimethyl ether by chlorination see (9) (10).]

[For use in production of halogenated higher ethers by addn. to olefins see (11).]

3:5245 (1) Regnault, *Ann.* 34, 31 (1840). (2) Brochet, *Ann. chim.* (7) 10, 297 (1897). (3) Grassi, Maselli, *Gazz. chim. ital.* 28, II 485 (1898). (4) Litterscheid, *Ann.* 330, 116 (1903). (5) Böhme, *Ber.* 74, 248–256 (1941), *C.A.* 35, 3972–3973 (1941) ... *J. Chem. Soc.* 117, 513–515 (1920). (7) Carr, *J. Soc. Chem. In*... *Angew. Chem.* 51, 271 (1938). (9) Salzberg, Werntz (to du P... *C.A.* 31, 1046 (1937), *Cent.* 1937, I 3715. (10) Booth (to ... 2,066,905, Jan. 5, 1937, *C.A.* 31, 1037 (1937); *Cent.* 1937, I 3529.
(11) Scott (to du Pont), U.S. 2,024,749, Dec. 17, 1935, Brit. 423,520, *C.A.* 30, 1067 (1936); *C.A.* 29, 4374 (1935).

3:5270 1,1,1-TRICHLOROPROPANE $CH_3.CH_2.CCl_3$ $C_3H_5Cl_3$ Beil. S.N. 10

("Ethylchloroform")

B.P. 106.5–108.5° (1)	$D_4^{23} = 1.287$ (1)
106–107° (1) (2)	

[For prepn. from 1,1-dichloropropene-1 (3:5120) + HCl + $AlCl_3$ at 5–10° see (1) (2) (4).]

[The compd. listed in Beil. I-106 as $\bar{C}$ is erroneous (1) (3).]

3:5270 (1) Levine, Cass (to du Pont) ... II 1572. (2) Levine, Cass (to du ... (3) Van Arkel, *Rec. trav. chim.* 51, ... (1942).

3:5275 CHLOROMETHYL CHLOROFORMATE $C_2H_2O_2Cl_2$ Beil. III —
(Chlorometbyl chlorocarbonate) $ClCH_2—O—C{=}O$ III_1-(6)
$|$ III_2-(11)
Cl

B.P. 106.5–107° at 760 mm. (1)		$D^{15}_{-} = 1.465$ (1)	$n^{22}_{D} = 1.4286$ (2)
107°	(8)		
106.5°	(2)		
104–107°	(3)	$D^{14}_{-} = 1.456$ (2)	
52.5–53° at 100 mm.	(1)		

See also text.

[*See also dichloromethyl chloroformate* (3:5315).]

Colorless lachrymatory oil. — Note that C̄ cannot by distillation be completely separated from dichloromethyl chloroformate (3:5315); the constants listed above are on samples contg. (1) about 9% of the latter, or (3) about 7% of dichloromethyl chloroformate + 2% dimethyl carbonate.

A mixt. of C̄ with dichloromethyl chloroformate (3:5315) has been employed as a chem. warfare agent under the names "K-Stoff," "Palite" (6). — [For studies of physiological action see (4) (5); for action on plant tissue see (7).]

[For prepn. of C̄ from methyl chloroformate (3:5075) or from methyl formate (1:1000) with Cl_2 under various conditions see (1) (2) cf. (6) (8) (9).]

C̄ with aq. at ord. temp. or more rapidly on boilg. or C̄ with aq. alk. in cold undergoes hydrolysis (1) yielding formaldehyde (1:0145) + 2 HCl + CO_2; by detn. via oxidn. with I_2 + NaOH of the formaldehyde so produced C̄ may be quant. estimated cf. (10) (6); note also that this hydrolysis to formaldehyde distinguishes C̄ from various other closely related compounds, e.g., methyl chloroformate (3:5075), dichloromethyl chloroformate (3:5315), trichloromethyl chloroformate ("Diphosgene") (3:5515), trichloromethyl trichloroacetate (3:0290), *bis*-(trichloromethyl) carbonate ("Triphosgene") (3:1915), or phosgene (3:5000).

C̄ (1 mole) with NaI (2 moles) in dry acetone at 20° (11) liberates I_2 also yielding formaldehyde (1:0145) + CO, but the reaction is *not* quantitative proceeding only to about 70% theoretical (11); but C̄ with dry NaI at 90–100° gives (1) CO + CO_2. Note that C̄ with LiBr in dry acetone does *not* (11) liberate bromine; in this respect C̄ is like methyl chloroformate (3:5075) but different from dichloromethyl chloroformate (3:5315) and trichloromethyl chloroformate ("Diphosgene") (3:5515).

[C̄ with $FeCl_3$ or $AlCl_3$ dec. rapidly at 70° (1) (12) yielding phosgene (3:5000) and formaldehyde (1:0145).]

[C̄ with methyl hydrogen sulfate gives (13) methyl chlorosulfonate, formaldehyde, CO_2 + HCl; C̄ with chlorosulfonic acid at 100° for 4 hrs. gives (13) chloromethyl chlorosulfonate + CO_2 + HCl; C̄ with dimethyl sulfate gives (78% yield (13)) methyl chlorosulfonate.]

[C̄ with alcohols or C̄ with alkali salts of phenols reacts as an acid chlorine yielding (6) the corresp. alkyl or aryl chloromethyl carbonates (1).]

[C̄ with K phenylcyanamide also reacts as an acid chloride giving (14) chloromethyl *N*-cyano-*N*-phenylcarbamate, m.p. 48°.]

3:5275 (1) Kling, Florentin, Lassieur, Schmutz, *Compt. rend.* **169**, 1046–1047 (1919); *Ann. chim.* (9) **13**, 44–59 (1920). (2) Grignard, Rivat, Urbain, *Compt. rend.* **169**, 1074–1077 (1919); *Ann. chim.* (9) **13**, 246–248 (1920). (3) Herbst, *Kolloidchem. Beihefte*, **23**, 330–331 (1927). (4) van Nieuwenberg, *Chem. Weekblad* **19**, 328 (1922). (5) Fegler, *Compt. rend. soc. biol.* **100**, 222–224

[For use as soil disinfectant of the mixt. of C̄ with 1,2-dichloropropene obtd. in manufacture of allyl chloride by chlorination of propylene see (15); for use of C̄ in prepn. of cellulose ethers see (16).]

Reactions involving unsaturated linkage of C̄. [C̄ with Cl_2 adds 1 mole halogen yielding (14) 1,1,2,3-tetrachloropropane (3:6035), b.p. 179–180° cor. at 756.6 mm. (14).] — C̄ with Br_2 adds 1 mole halogen giving (72.7% yield (9)) (5) (3) (17) 1,2-dibromo-1,3-dichloropropane [Beil. I-112], b.p. 212° (3), 215–217° (9), 220–221° (17), 220–225° (5).

[C̄ with fumg. HCl in s.t. at 150° blackens but does not add HCl (5).]

Reactions involving the one reactive chlorine atom of C̄. Note that the 2 chlorine atoms in C̄ possess very different reactivities; that attached to the carbon directly connected with the double bond is inert, while the chlorine attached to the carbon in β-relationship to the unsaturated linkage is extremely reactive.

[C̄ with aq. KOH (1 mole) boiled for 30 hrs. (14), or boiled with 10% aq. Na_2CO_3 (slight excess) for 2 hrs. (1), or shaken with aq. silver oxide at room temp. for 24 hrs. (small yield (12)) gives 3-chloropropen-2-ol-1 (1-chloropropen-1-ol-3) (γ-chloroallyl alcohol) (3:5820); note that the high-boilg. stereoisomer of C̄ gives (76% yield (1)) the high-boilg. stereoisomer of the resultant alc., while the low-boilg. stereoisomer of C̄ gives (81% yield (1)) the low-boilg. stereoisomer of the resultant alc.; note also that aq. NaOH effects from the resultant γ-chloroallyl alc. the removal of HCl and also causes polymerization (1) so that use of hydrolytic conditions as mild as possible is desirable.] — [For reactn. of C̄ with NaSH or Na_2S see (18).]

[C̄ with Na alcoholates, NaOR, replaces the reactive chlorine atom by the alkoxy residue yielding ω-chloroallyl alkyl ethers of general formula RO—CH_2—CH=CHCl: e.g., C̄ with NaOMe refluxed 4 hrs. gives (12) 1-chloro-3-methoxypropene-1, b.p. 107–108°, $D^{27}_{-} = 1.032$, $n^{27}_{-} = 1.431$ (12) (note proximity of b.p. to that of ord. C̄) (for study of kinetics of this reactn. see (19)); C̄ with NaOEt refluxed for 4 hrs. (12) or C̄ with alc. KOH (5) yields 1-chloro-3-ethoxypropene-1 [Beil. I-439], b.p. 126–127°, $D^{16}_{-} = 1.018$, $n^{16}_{-} = 1.438$ (12); for corresp. reactns. of C̄ with Na derivs. of benzyl alc. (1:6480), β-phenylethyl alc. (1:6505), γ-phenyl-*n*-propyl alc. (1:6520), and cinnamyl alc. (1:5920) together with physical consts. of prods. see (20).]

[C̄ with alkali metal phenolates replaces the reactive chlorine atom by the aryloxy residue yielding ω-chloroallyl aryl ethers of general formula $RO.CH_2.CH=CHCl$: e.g., C̄ with Na phenolate in abs. alc. refluxed ½ hr. (21), or C̄ with phenol (1:1420) + dry K_2CO_3 in boilg. acetone (8), gives (yields: 75% (21), 72% (8)) ω-chloroallyl phenyl ether, b.p. 120–121° at 20 mm. (21), 122–127° at 27 mm. (8), $D^{15}_{4} = 1.146$ (21), $n^{20}_{D} = 1.5421$ (8), $n^{15}_{D} = 1.5447$ (21); for corresp. reactn. with salts of *o*-cresol (1:1400) (21), *m*-cresol (1:1730) (21), *p*-cresol (1:1410) (21) (8), carvacrol (1:1760) (21), thymol (1:1430) (21), β-naphthol (1:1540) (21), hydroquinone (1:1590) (21), and several other phenols (21) see indic. refs. — Note that these ω-chloroallyl aryl ethers upon treatment with Br_2 do *not* add halogen to the unsatd. linkage but instead undergo cleavage: e.g., ω-chloroallyl phenyl ether (above) in $CHCl_3$ with Br_2 (1 mole) at 0° yields (22) phenol (1:1420) + *p*-bromophenol + 3-bromo-1-chloropropene-1 (see below) + ω-chloroallyl *p*-bromophenyl ether, b.p. 153° at 13 mm., $D^{11}_{4} = 1.521$, $n^{11}_{D} = 1.5785$ (22). — Note furthermore that these ω-chloroallyl aryl ethers with HBr or HI do *not* add hydrogen halide to the unsaturated side chain but instead undergo cleavage similar to that with halogens: e g., ω-chloroallyl phenyl ether in AcOH with HBr gas (1 mole) gives (70% yield (23)) 3-bromo-1-chloropropene-1, lachrymatory oil, b.p. 130° at 760 mm., $D^{9.5}_{4} = 1.670$, $n^{9.5}_{D} = 1.5255$ (23); similarly action of HI yields (23) 1-chloro-3-iodopropene-1, lachrymatory oil, b.p. 162° at 760 mm. sl. dec., 58° at 19 mm., $D^{9.5}_{4} = 2.029$, $n^{9.5}_{D} = 1.5993$ (23).]

[C̄ with phenols under suitable conditions can also react to effect direct nuclear alkenyla-

tion: e.g., $\bar{C}$ with phenol (1:1420) + Na in C_6H_6 refluxed for 17 hrs. gives (17% yield (8)) o-(γ-chloroallyl)phenol, b.p. 151–156° at 31 mm., $n_D^{23} = 1.5638$ (8) (soluble in alk.), accompanied by some ω-chloroallyl phenyl ether (insol. alk.) (see above).]

[$\bar{C}$ with phenol ethers undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the ω-chloroallyl group into the aromatic nucleus: e.g., $\bar{C}$ (1 mole) with anisole (1:7445) (10 moles) + $AlCl_3$ gives (70% yield (24)) 1-(ω-chloroallyl)-4-methoxybenzene, b.p. 126° at 15 mm. (24); $\bar{C}$ (1 mole) with pyrocatechol dimethyl ether (veratrole) (1:7560) (2 moles) + Zn dust (1 g.) ($AlCl_3$ unsuitable) gives 1-(ω-chloroallyl)-3,4-dimethoxybenzene, b.p. 162° at 15 mm., $D_4^{14} = 1.168$, $n_D^{14} = 1.551$ (24); $\bar{C}$ with pyrogallol trimethyl ether (1:7145) similarly yields 1-(ω-chloroallyl)3,4,5-trimethoxybenzene, b.p. 174° at 15 mm., $D_4^{18} = 1.176$, $n_D^{18} = 1.539$ (24). — Note that such ω-chloroallyl aryl ethers (1 mole) upon treatment with KOH (3 moles) in an alcohol R′.OH (5 moles) give (by reactn. of the ω-chlorine and rearr. or vice versa) substituted cinnamyl ethers of the type $RO.C_6H_4.CH=CH.CH_2OR'$, used for prepn. of various natural prods. (24).]

[$\bar{C}$ with aromatic hydrocarbons undergoes Friedel-Crafts reactn. of the reactive halogen atom with resultant introduction of the ω-chloroallyl group into the aromatic nucleus e.g., $\bar{C}$ with C_6H_6 + $AlCl_3$ yields (25) γ-chloroallylbenzene (1-chloro-3-phenylpropene-1) (3:8737) (see below); for analogous reactions of $\bar{C}$ with toluene (1:7405), o-xylene (1:7430), m-xylene (1:7420), p-xylene (1:7415), ethylbenzene (1:7410), cumene (1:7440), pseudocumene (1:7470), mesitylene (1:7455), p-cymene (1:7505), etc., see (25). — Note that the resultant γ-chloroallyl hydrocarbons add Br_2 normally (26) to the unsatd. linkage (diff. from ω-chloroallyl aryl ethers (above) which undergo cleavage); e.g., γ-chloroallylbenzene (above) with Br_2 gives γ-chloro-β,γ-dibromo-n-propylbenzene, b.p. 160° at 12 mm., $D_4^{10} = 1.727$, $n_D^{10} = 1.611$ (26) (for use of this prod. in prepn. of hydrocinnamaldehyde (1:0225) see (35).)]

[The direct actn of $\bar{C}$ with NH_3 appears to be unreported; however, $\bar{C}$ with KSCN followed by alk. hydrolytic cleavage is claimed (27) to yield the expected γ-chloroallylamine. — $\bar{C}$ with methylamine (3 moles) in C_6H_6 gives (53% yield (28)) N-methyl-γ-chloroallylamine [Beil. IV₂-(668)], b.p. 125° ($\bar{B}$.PkOH, m.p. 91° (28)), accompanied by a little N-methyl-bis-(γ-chloroallyl)amine [Beil. IV₂-(668)], b.p. 88° at 16 mm. (28). — $\bar{C}$ with diethylamine reacts vigorously and on making alkaline gives (75% yield (29)) (12) N,N-diethyl-γ-chloroallylamine [Beil. IV₂-(668)], b.p. 57–58° at 17 mm. (12), 55° at 9 mm. (29) ($\bar{B}$.HCl, pl. from acetone, m.p. 221° (29); $\bar{B}$ PkOH, ndls. from aq., m.p. 78° (29), 91° (12); $\bar{B}.H_2PtCl_6$, m p 169–170° (12)). — For reactns. of $\bar{C}$ with tertiary amines, e.g., with Me_3N (29), Et_3N (29), or pyridine (19), see indic. refs.]

[$\bar{C}$ (1 mole) with aniline (2 moles) in C_6H_6 under reflux ppts. aniline hydrochloride and from the solvent gives (68% yield (30)) N-phenyl-γ-chloroallylamine, b.p. 137° at 13 mm., $D_4^{13} = 1.1456$, $n_D^{13} = 1.590$ (30); for analogous reactns. of $\bar{C}$ with o-toluidine and m-toluidine see (30).]

[$\bar{C}$ with excess $CaBr_2$ refluxed for 40 hrs. (12) or actn. of HBr on ω-chloroallyl aryl ethers (23) (discussed above) gives (58% yield (12)) 3-bromo-1-chloropropene-1 (consts. given above); similarly $\bar{C}$ with excess powdered CaI_2 shaken at room temp. for 20 hrs. gives (65% yield (12)) (14) 1-chloro-3-iodopropene-1 (consts. given above).]

[$\bar{C}$ with NaOAc in AcOH at 110° for 16 hrs. ppts. NaCl (70% theory (12)) and gives (50% yield (12)) γ-chloroallyl acetate [Beil. II-136], b.p. 156–159° (10), b.p. 57° at 15 mm., $D_-^{17} = 1.140$, $n_-^{17} = 1.444$ (12).]

$\bar{C}$ reacts very slowly if at all with most metals: e.g., $\bar{C}$ with Zn dust in boilg. acetone or C with Mg in dry ether (even in pres. of I_2, EtBr, or $HgCl_2$) is inert (12); however, $\bar{C}$ with Na in tetralin (1:7550) reacts violently giving only gaseous products (12), possibly including allene (propadiene-1,2) cf. (3) (31).

[$\bar{C}$ reacts readily with aryl MgBr cpds., with replacement of its active halogen atom by the aryl radical: e.g., $\bar{C}$ with C_6H_5MgBr in toluene (26) or ether (32) gives (alm. 100% yield (26)) γ-chloroallylbenzene (1-chloro-3-phenyl-propene-1 (3:8737), b.p. 76° at 13 mm. (32), D_4^{14} = 1.073 (26), n_D^{14} = 1.545 (26). — For analogous reactns. of $\bar{C}$ with *o*-tolyl-, *p*-tolyl-, *p*-cumyl-, 2-cymyl-, *p*-bromophenyl-, and *p*-methoxyphenyl-MgX cpds. see (26); for corresp. reactn. of $\bar{C}$ with α-naphthyl MgBr see (34). — For reactn. of $\bar{C}$ with *n*-propyl MgBr see (2).]

[For reactn. of $\bar{C}$ with diethyl sodiomalonate giving (26% yield (4)) diethyl γ-chloroallylmalonate, with diethyl disodiomalonate giving (32% yield (4)) diethyl *bis*-(γ-chloroallyl)malonate, or with diethyl sodio-ethyl-malonate giving (20% yield (4)) diethyl γ-chloroallyl-ethyl-malonate see indic. refs.]

3:5280 (1) Hatch, Moore, *J. Am. Chem. Soc.* **66**, 285–287 (1944). (2) Kirrmann, Grard, *Compt. rend.* **190**, 876–878 (1930). (3) Hartenstein, *J. prakt. Chem.* (2) **7**, 308–314 (1873). (4) Hill, Fischer, *J. Am. Chem. Soc.* **44**, 2582–2595 (1922). (5) Friedel, Silva, *Compt. rend.* **75**, 81–85 (1872). (6) Bon, *Uchenye Zapiski Leningrad Gosudarst Univ., Ser. Khim. Nauk.* **3**, 3–37 (1938); *Cent.* **1939**, II 366; *C.A.* **33**, 3755 (1939). (7) Bert, Dorier, *Bull. soc. chim.* (4) **39**, 1573–1575 (1926). (8) Hurd, Webb, *J. Am. Chem. Soc* **58**, 2191–2193 (1936). (9) Földi, *Ber.* **60**, 659–660 (1927). (10) Martinoff, *Ber.* **8**, 1318–1319 (1875).

(11) Berthelot, Luca, *Ann. chim.* (3) **52**, 437–438 (1858). (12) Kirrmann, Pacaud, Dosque, *Bull. soc. chim.* (5) **1**, 860–871 (1934). (13) Reboul, *Ann. chim.* (3) **60**, 37–38 (1860). (14) van Romburgh, *Bull. soc. chim.* (2) **36**, 549–557 (1881); (2) **37**, 98–103 (1882). (15) Carter, *Science* **97**, 383–384 (1943). (16) du Pont Co., Brit 429,949, July 11, 1935; *Cent.* **1936**, I 4098, *C.A.* **29**, 7073 (1935). (17) Reboul, *Ann. Suppl.* **1**, 231 (1861). (18) Lilienfeld, French 758,359, Jan. 15, 1934; *Cent.* **1934**, I 3653. (19) Tronow, Gerschewitsch, *J. Russ. Phys.-Chem. Soc.* **59**, 727–739 (1927), *Cent.* **1928**, I 2924. (20) Dorier, *Compt rend.* **196**, 1325–1327 (1933).

(21) [illegible] (1931); *Cent.* **1931**, II 2318. (22) Bert, Andor, *Compt.* [illegible] I 3429. (23) Bert, Andor, *Compt. rend.* **194**, 722–724 [illegible] *Compt. rend.* **213**, 797–798 (1941); *Cent* **1942**, II 1564; [illegible] *rend* **213**, 619–620 (1941); *Cent* **1942**, II 30; *C.A.* **37**, 4373 (1943). (26) Bert, *Bull soc.* [illegible] (1925). (27) I.G., Dutch 52,449, M[illegible] Weismantel, *Ann.* **449**, 254–265 (1926). (29) Ingold, Rothstein, *J. Chem. Soc.* **1929**, 11–12. (30) Dorier, *Compt. ren*[illegible]

(31) Béhal, *Ann. chi*[illegible]
(33) Bert, Dorier, *Com*[illegible]
(34) Bert, Dorier, *Bull. soc. chim.* (4) **37**, 1600–1602 (1925). (35) Bert, *Compt. rend.* **215**, 356–357 (1942); *C.A.* **38**, 3633 (1944).

3:5290 DICHLOROACETYL CHLORIDE $Cl_2CH.C(Cl){=}O$ C_2HOCl_3 Beil. II - 204
II_1-(92)
II_2-(196)

B.P.	108°	(1)
	107–108°	(2)
	105–107°	(3) (4)
	106.1–107.1° at 739 mm.	(5)

Oil with penetrating odor; fumes in moist air.

[For prepn. of $\bar{C}$ from dichloroacetic acid (3:6208) with PCl_3 (2), with HCl gas + P_2O_5 (7), with $SOCl_2$ (poor yield apparently because of much formation (9) of dichloro-acetic anhydride (3:6430)) (8) (9) (10) (11), with benzoyl chloride (3:6240) (73% yield (4)), or with benzotrichloride (3:6540) (12) (13) see indic. refs.; for prepn. of $\bar{C}$ from trichloroethylene (3:5170) by photochemical oxidn. (14) (15) (16) (3) (17) see indic. refs.; for prepn. of $\bar{C}$ from pentachloroethane (3:5880) with fumg. H_2SO_4 at 50–60° see (18); for prepn. of $\bar{C}$ from α,β-dichlorovinyl ethyl ether (3:5540) by actn. of Cl_2 see (19) (20).]

[$\bar{C}$ with alcohols gives corresp. esters (for studies of rate of alcoholysis see (1) (21)); for reactn. of $\bar{C}$ with various carbohydrates (22) and with cellulose (23) see indic. refs.; $\bar{C}$ + phenol yields (20) phenyl dichloroacetate, m.p. 48°, b.p. 247.5° cor. (20); $\bar{C}$ with β-naphthol yields (20) β-naphthyl dichloroacetate, m.p. 92–93° (20).]

[$\bar{C}$ on warming with $AlCl_3$ yields (24) (25) 1,1,1,2,2,3,3-heptachloropropane (3:0200) + chloroform (3:5050) + CO + HCl]

[$\bar{C}$ treated with dry HI gas at −5° gives (58% yield (5)) dichloroacetyl iodide, b.p. 54–54.5° at 15 mm. (5).]

$\bar{C}$ with aq. hydrolyzes very rapidly yielding dichloroacetic acid (3:6208) q.v.; for the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{C}$ see dichloroacetic acid (3:6208).

3:5290 (1) Branch, Nixon, *J Am. Chem Soc* **58**, 2499–2504 (1936) (2) Otto, Beckurts, *Ber.* **14**, 1618–1619 (1881). (3) Erdmann, *J prakt. Chem.* (2) **85**, 78–89 (1912). (4) Brown, *J. Am. Chem Soc* **60**, 1325–1328 (1938). (5) Gustus, Stevens, *J. Am. Chem. Soc.* **55**, 374–377 (1933). (6) Vanderstichele, *J Chem Soc.* **123**, 1228 (1923). (7) Frankland, Patterson, *J. Chem Soc.* **73**, 187 (1898). (8) Boeseken, *Rec. trav. chim* **29**, 99–100 (1910). (9) Blaise, *Bull. soc chim.* (4) **15**, 729 (1914) (10) Carré, Libermann, *Compt. rend* **199**, 1423 (1934).

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(21) Leimu, *Ber.* **70**, 1046 (1937) (22) Bell, *J. Chem. Soc* **1935**, 1180–1182. (23) Barnett, *J. Soc. Chem. Ind.* **40**, T-253–256, 274 (1921) (24) Ref. 8, p. 108. (25) Böeseken, Prins, *Cent.* **1911**, I 466.

3:5300 1,1-DICHLORO-2-METHYLPROPENE-1 CH_3 $C_4H_6Cl_2$ Beil. I-209
(α,α-Dichloroisobutylene) $H_3C-\overset{|}{C}=CCl_2$ I_1— I_2—

B.P. **108.7–109.1°** (1) D_0^{20} = **1.449** (3)
108–109° (2)
107.5–108.5° (3)

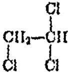
Note: $\bar{C}$ by virtue of allylic transposition may yield derivatives of its synionic isomer 1,3-dichloro-2-methylpropene-1 (3·5590) q v.

[For prepn. of $\bar{C}$ from β,β,β-trichloro-*ter*-butyl acetate (3:6180) (85% yield (3) (2)) or from β,β,β-trichloro-*ter*-butyl alcohol ("Chloretone") (3:2662) (very poor yield (1)) with Zn dust in alc. see (1) (2) (3); for prepn. of $\bar{C}$ from 1,1,1-trichloro-2-bromo-2-methylpropane by htg. in quinoline (2), or from 1,1,1,2-tetrachloro-2-methylpropane (3:4725) by htg. with K in tetralin (5% yield (2)), see (2).]

$\bar{C}$ with Br_2 yields (2) 1,2-dibromo-1,1-dichloro-2-methylpropane, m.p. 209° (s.t.) (2).

3:5300 (1) Bruyne, Davis, Gross, *Physik. Z.* **33**, 720 (1932). (2) Jacob, *Bull. soc. chim.* (5) **7**, 581–586 (1940); *C.A* **36**, 3507 (1942). (3) Favorskii, Jozitsch, *Cent.* **1899**, I 778. (4) Jozitsch, *Cent.* **1899**, I 606.

3:5330 1,1,2-TRICHLOROETHANE (*unsym.*-Trichloroethane, chloroethylidene (di)chloride)



$C_2H_3Cl_3$ Beil. I - 85, I_1-(24), I_2-(55)

B.P.			F.P.		
[114.2° at 757.7 mm. (1)]	−37.4° (8)	D_4^{25} = 1.4345 (13)	n_{He}^{25} = 1.47345 (7)
114° at 767 mm. (13)	−36.6° (11)		
114° at 760 mm. (2)	−35.5° (5)	D_4^{20} = 1.443 (2)	n_D^{20} = 1.4708 (12)
113.72° at 760 mm. (3)		1.4416 (13)	1.47064 (8)
113.65° at 760 mm. (4)		1.4411 (8)	
113.5° at 760 mm. (5) (6)			
113.5° (7)			
113.3° cor. at 760 mm. (8)			
113.2° (9)			
112.5-113° (10)			

Care must be taken to avoid confusion of C̄ with the isomeric *1,1,1-trichloroethane* (3:5085). C̄ is now comml. prod. in U.S. (14).

MISCELLANEOUS PHYSICAL PROPERTIES

[illegible] sol. aq.: e.g., 100 g. aq. at 0° dis. 0.460 g. [illegible] g. C̄ (15). — [For soly. of aq. in C̄ at 0°, [illegible] (16).] [illegible] d press. see (10).] [For soly. of I_2 in C̄ see (17).]

Binary systems contg. C̄. (See also below under uses of C̄.) C̄ + 1,2-dichloroethane (ethylene dichloride) (3:5130): for f.p./compn. data, eutectic f.p. −70° (11), and for D and vapor/liq. equil. (13), see indic. refs.

Azeotropes contg. C̄. C̄ with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 77.8° (4), 77.3° (6) at 760 mm., contg. 35 (6), 30 (4) wt. % C̄.

Other physical props. [For study of thermal conductivity of C̄ see (18).]

USES OF C̄

C̄ is now widely used as industrial solvent and in other ways [e.g., for use of C̄ (10%) 1,1,1-trichloroethane (3:5085) + 20% pet. hydrocarbons as dry-cleaners' solv. see (19); for use of C̄ + ethylene dichloride (3:5130) as hair wash see (20); for use of C̄ + n-heptane (1:8575), C̄ + cyclohexane (1:8405), or C̄ + C_6H_6 (1:7400) as test mixts. for detn. of number of theoret. pl. in fractionating columns see (21); for use of C̄ in dewaxing of oils see (22)].

PHYSIOLOGICAL ACTION AND TOXICITY

Full treatment of this topic is beyond the scope of this work [however, for lead references see (23) (24) (25) (26) (27) (67). — For study of C̄ as anthelmintic see (28)].

PREPARATION OF C̄

From vinyl chloride (3:7010). (See also below under acetylene.) [For prepn. of C̄ from vinyl chloride with Cl_2 at 0-80° in light or at 180-250° in absence of light or solv. see (29) (30) (31) cf. (32); for study of photochemical addn. of Cl_2 to vinyl chloride yielding C̄ see (33).]

From 1,2-dichloroethylene (3:5030). [For prepn. of C̄ from 1,2-dichloroethylene by addn. of HCl gas at 30-40° in pres. of $AlCl_3$ (88% yield) see (34) (37) (note that 1,1,2,3,4-pentachlorobutane (3:0750) is also obtd. as a by-product (35)).]

From 1,1-dichloroethane (ethylidene (di)chloride) (3:5035). [For formn. of C̄ from ethylidene (di)chloride with $SbCl_5$ (3 wt. parts) on refluxing see (36).]

From 1,2-dichloroethane (ethylene (di)chloride) (3:5130). [For prepn. of C̄ from ethylene (di)chloride with Cl_2 in ultra-violet light at 50° (38) (39) or 25° (40), or with Cl_2 + suitable cat. at not above 60° (41), or C̄ (as liquid) with Cl_2 (7), or with Cl_2 in pres. of $AlCl_3/NaCl/FeCl_3$ at 300–425° as directed (42), or with SO_2Cl_2 + trace dibenzoyl peroxide refluxed 2 hrs in dark (12) (yields: 80% (41), 70% (40) (12), 50% (42)), see indic. refs.]

From ethylene. [For prepn. or formn. of C̄ from ethylene with Cl_2 + cat. see (43) (44) (45) (46) (47).]

From acetylene. [For prepn. of C̄ from acetylene with HCl + Cl_2 + cat. (doubtless via formn. of vinyl chloride (and subsequent addn. of Cl_2 as above) see (48) (30).]

From other sources. [For formn. of C̄ as by-prod. of prepn. of chloral (3:5210) see (49); for prepn. of C̄ from 2,2-dichloroethanol-1 (3:5745) with PCl_5 (50), or from α,β-dichloroethyl chloroformate by loss of CO under influence of $AlCl_3$ (51), see indic. refs.; for formn. of C̄ from trichloroethylene (3:5170) with HI for 2 weeks in sunlight see (68).]

CHEMICAL BEHAVIOR OF C̄

Dehydrochlorination. C̄ under suitable conditions may lose HCl in either or both of two modes yielding either or both 1,1-dichloroethylene (vinylidene (di)chloride) (3:5005) *or a mixt. of the stereoisomeric 1,2-dichloroethylenes* (3:5030). — [E.g., C̄ with alc. KOH (52) (53) (54), or with excess aq. $Ca(OH)_2$ at 70–80° (55) (56), or with aq. or alc. NH_3 (57), or even with Na in ether (58) gives (yields 100% (57), 90% (55) (56)) 1,1-dichloroethylene (3:5005). — On the other hand, C̄ pyrolyzed at 400° over pumice contg. $CuCl_2$ (59) is claimed to give mainly 1,2-dichloroethylene (3:5030). — Note also that C̄ with MeOH over Al_2O_3 at 290° gives (60) a mixt. of both prods. together with MeCl (3:7005).]

[Note in this connection that C̄ with aq. + Zn, Fe, or Al at 100–120° under press. yields (61) vinyl chloride (3:7010); perhaps this occurs by way of the above dichloroethylenes as intermediate.]

Halogenation of C̄. *Chlorination.* [C̄ with Cl_2 + $AlCl_3$ at 70–80° yields (62) 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750).]

Fluorination. [C̄ with HgF_2 under press. at 140° gives (63) 50% 1,2-dichloro-1-fluoroethane + 10% 2-chloro-1,1-difluoroethane; for behavior of C̄ with SbF_3 + Br_2 at 160°, with SbF_3 + $SbCl_5$, or with SbF_3Cl_2 see (63).]

Behavior of C̄ with other inorganic reactants. [C̄ with alkali hydroxide on fusion at 250–300° yields (64) salts of glycolic acid (1:0430).]

Behavior of C̄ with organic reactants. [C̄ with 1,2-dichloroethylene (3:5030) + 1% $AlCl_3$ at 35–40° for 5 days yields (37) a mixt. of two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., the liq. isomer (3:9068) and the solid isomer (3:0750). — C̄ + trichloroethylene (3:5170) + 1–2% $AlCl_3$ at 40° for 7 days yields (37) 1,1,1,4,4-pentachlorobutene-2 (3:9054).]

[C̄ with C_6H_6 + $AlCl_3$ gives (31% yield (65)) 1,1,2-triphenylethane, b.p. 211° at 14 mm., accompanied by diphenylmethane and 1,2-diphenylethylene (stilbene).]

[*C̄ with C_6H_5MgBr in toluene does* ***not*** react even at 100° (66).]

Comment on Fujiwara reaction. C̄ does *not* respond to Fujiwara reactn. (pyridine + NaOH) (23).

3:5330 (1) Pierre, *Ann.* **80**, 127 (1851). (2) Mumford, Phillips, *J. Chem. Soc.* **1928**, 159. (3) Staedel, *Ber.* **15**, 2563 (1882). (4) Lecat, *Ann. soc. sci. Bruxelles* **47**, I, 112 (1927); *Cent.* **1927**, II 1677. (5) Timmermans, *Bull. soc. chim. Belg.* **27**, 334–343 (1913); *Cent.* **1914**, I 618. (6)

Lecat, "L'Azeotropisme," 1918, p. 84. (7) Hamai, *Bull. Chem. Soc. Japan* **9**, 542–548 (1934). (8) Henne, Hubbard, *J. Am. Chem. Soc.* **58**, 404 (1936). (9) Kohlrausch, Köppl, *Monatsh.* **65**, 197 (1935). (10) Hamai, *Bull. Chem. Soc. Japan* **10**, 207–211 (1935).

(11) Timmermans, Vesselovsky, *Bull. soc. chim. Belg.* **40**, 505 (1931). (12) Kharasch, Brown, *J. Am. Chem. Soc.* **61**, 2145 (1939). (13) Portnov, Selerovich, *Trans. State Inst. Applied Chem. (U.S.S.R.)* **24**, 81–89 (1935); not in *Cent.*; *C.A.* **29**, 7272 (1935). (14) McLure, *Chem. Eng. News* **22**, 421 (1944). (15) van Arkel, Vles, *Rec. trav. chim.* **55**, 410 (1936). (16) Staverman, *Rec. trav. chim.* **60**, 836–841 (1941); *Cent.* **1942**, I 1352; *C.A.* **37**, 2638 (1943). (17) Margosches, Hinner, Friedmann, *Z. anorg. allgem. Chem.* **137**, 87–90 (1924). (18) Bates, Hazzard, Palmer, *Ind. Eng. Chem.* **33**, 375–376 (1941). (19) Parkhurst (to Standard Oil of California), U.S. 1,948,045, Feb. 20, 1934; *Cent.* **1934**, II 863; *C.A.* **28**, 2924 (1934). (20) Cathala, French 598,518, Dec. 18, 1925; *Cent.* **1926**, I 2752, not in *C.A.*

(21) Stage, Schultze, *Oel u. Kohle* **40**, 90–95 (1944); *C.A.* **38**, 6131 (1944). (22) Sharples Specialty Co., French 801,583; Aug. 7, 1936; *Cent.* **1937**, I 263; *C.A.* **31**, 635 (1937). (23) Barrett, Cunningham, Johnston, *J. Ind. Hyg. Toxicol.* **21**, 479–480 (1939). (24) von Oettingen, *J. Ind. Hyg. Toxicol.* **19**, 398–399 (1937). (25) Schwander, *Arch. Gewerbepathol. Gewerbehyg.* **7**, 109–116 (1936); *Cent.* **1939**, II 1331; not in *C.A.* (26) Barsoum, Saad, *Quart. J. Pharm. Pharmacol.* **7**, 205–214 (1934); *Cent.* **1934**, II 2550; *C.A.* **28**, 6194 (1934). (27) Lazarev, *Arch. exptl. Path. Pharmakol.* **141**, 19–24 (1929); *Cent.* **1929**, II 451, *C.A.* **25**, 3074 (1931). (28) Wright, Schaffer, *Am. J. Hyg.* **16**, 372–374 (1932). (29) Ernst, Lange (to I.G.), U.S. 1,833,358, 1,833,393, Nov. 24, 1931; *C.A.* **26**, 1301 (1932): Ger. 489,454, Jan. 17, 1930; [*Cent.* **1930**, I 3829; *C.A.* **24**, 2145 (1930)]: Brit. 298,084, Nov. 28, 1928, *Cent.* **1929**, I 1396; *C.A.* **23**, 2724 (1929). (30) I.G., French 690,655, Sept. 24, 1930; *Cent.* **1931**, I 1164; *C.A.* **25**, 1264 (1931): Brit. 349,097, March 11, 1929; *C.A.* **26**, 5314 (1932); not in *Cent.*

(31) Consortium für Elektrochem. Ind., French 690,767, Sept. 25, 1930; *Cent.* **1931**, I 1164; *C.A.* **25**, 1264 (1931). (32) Biltz, *Ber.* **35**, 3526–3527 (1902). (33) Schmitz, Schumacher, *Z. physik. Chem.* **B-52**, 73–80 (1942). (34) Prins, *Rec. trav. chim.* **45**, 80–81 (1926). (35) Müller, Hönn, *J. prakt. Chem.* (2) **133**, 289–290 (1932). (36) Meyer, Müller, *J. prakt. Chem.* (2) **46**, 174–175 (1892). (37) Prins, *Rec. trav. chim.* **56**, 119–125 (1937). (38) Coleman, Moore (to Dow Chem. Co.), U.S. 2,174,737, Oct. 3, 1939; *C.A.* **34**, 770 (1940). (39) Compagnie des Prod. Chim. d'Alais, etc., French 804,491, Oct. 24, 1936; *Cent.* **1937**, I 1545; *C.A.* **31**, 3500 (1937). (40) Maier, Ger. 522,959, April 20, 1931; [*Cent.* **1931**, I 3607]; *C.A.* **25**, 3670 (1931): French 655,939, April 25, 1929; *Cent.* **1929**, II 1347; *C.A.* **23**, 3934 (1929).

(41) Jung, Zimmermann, Ger. 545,993, March 8, 1932; *Cent.* **1932**, I 2893; *C.A.* **26**, 3520 (1932). (42) Reilly (to Dow Chem. Co.), U.S. 2,140,549, Dec. 20, 1938; *Cent.* **1939**, I 3625; *C.A.* **33**, 2540 (1939). (43) Gavat, *Ber.* **76**, 1115–1118 (1943); *C.A.* **38**, 4901 (1944). (44) Golov, *Sbornik Dikhloretan* **1939**, 18–20; *C.A.* **36**, 2523 (1942). (45) Bahr, Zieler, *Z. angew. Chem.* **43**, 233–236 (1930). (46) Stewart, Smith, *J. Am. Chem. Soc.* **51**, 3082–3095 (1929). (47) Askenasy, Heller, Ger. 549,341, April 26, 1932; *Cent.* **1932**, II 286; *C.A.* **26**, 3807 (1932). (48) I.G., French 687,307, Aug. 7, 1930; *Cent.* **1930**, II 3637; *C.A.* **25**, 715 (1931); Brit. 344,592, Jan. 31, 1929; *C.A.* **26**, 155 (1932); not in *Cent.* (49) Kraemer, *Ber.* **3**, 261 (1870). (50) Delacre, *Compt. rend.* **104**, 1186 (1887).

(51) Müller, *Ann.* **258**, 58 (1890). (52) Brockway, Beach, Pauling, *J. Am. Chem. Soc.* **57**, 2695 (1935). (53) Regnault, *J. prakt. Chem.* (1) **18**, 82–85 (1839); *Ann. chim.* (2) **69**, 155–159 (1838). (54) Klunont, *Chem. Ztg.* **46**, 521 (1922). (55) I.G., Brit. 349,872, July 2, 1931; *Cent.* **1931**, II 1191; *C.A.* **26**, 5314 (1932); French 702,361, April 7, 1931; *Cent.* **1931**, II 1191; *C.A.* **25**, 4285 (1931): Ger. 520,004, July 4, 1929; *C.A.* **25**, 5178 (1931); not in *Cent.* (56) Howell (to Imp. Chem. Ind., Ltd.), Brit. 531,733, March 17, 1941; *C.A.* **36**, 1336 (1942). (57) Engel, *Bull. soc. chim.* (2) **48**, 97 (1887). (58) Brunner, Brandenburg, *Ber.* **10**, 1497–1499 (1877); **11**, 61–62 (1878). (59) Hermann, Baum (to Consortium für Elektrochem. Ind.), U.S. 1,921,879, Aug. 8, 1933; [*C.A.* **27**, 5086 (1933)], not in *Cent.*: Ger. 570,954, Feb. 22, 1933; *C.A.* **27**, 4252 (1933); not in *Cent.*: French 694,054, Nov. 28, 1930; *Cent.* **1931**, I 1514; [*C.A.* **25**, 1843 (1931)]. (60) I.G., French 805,503, Nov. 21, 1936; *Cent.* **1937**, I 2258; [*C.A.* **31**, 4345 (1937)].

(61) I.G., Ger. 525,309, May 21, 1931; *Cent.* **1931**, II 1055; *C.A.* **25**, 4012 (1931): French 703,767, May 6, 1931; *Cent.* **1931**, II 1055; [*C.A.* **25**, 4557 (1931)]. (62) Taurikh, *Trans. State Inst. Applied Chem. (U.S.S.R.)* **24**, 77–80 (1935); *C.A.* **29**, 7272 (1935); not in *Cent.* (63) Henne, Renoll, *J. Am. Chem. Soc.* **58**, 889–890 (1936). (64) Strosacker, Pelton (to Dow Chem. Co.), U.S. 1,881,354, Oct. 25, 1932; *Cent.* **1933**, I 307; [*C.A.* **27**, 1006 (1933)]. (65) Bert, *Compt. rend.* **213**, 792–793 (1941); *Cent.* **1942**, II 1785; *C.A.* **37**, 4065 (1943). (66) Bert, *Bull. soc. chim.* (4) **41**, 1173 (1927). (67) Lehman, Schmidt-Kehl, *Arch. Hyg. Bakt.* **116**, 131–268 (1936); *C.A.* **31**, 477 (1937); not in *C.A.* (68) Kharasch, Norton, Mayo, *J. Org. Chem.* **3**, 48–50 (1938).

3:5345 3,3,3-TRICHLOROPROPENE-1 $Cl_3C{-}CH{=}CH_2$ $C_3H_3Cl_3$ **Beil. I-200**
(1,1,1-Trichloropropene-2) I_1— I_2—

B.P.	M.P.		
114–115° at 760 mm. (1)	**−30°** (2)	D_{20}^{20} = **1.369** (1)	n_D^{20} = **1.4827** (3)
114–115° at 757 mm. (2)	**−55– −50°** (1) (5)		(5)
57° at 103 mm. (3)		D_{13}^{13} = **1.359** (2)	

Liquid with penetrating odor suggesting aldehydes. [For use in dewaxing of mineral oil see (4).]

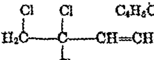
[For prepn. of C̄ from 1,1,1-trichloropropanol-2 (3·0846) (84% yield (3)) with P_2O_5 (3) (2) (1), with PCl_3 (5) (1), or with PCl_5 (5) (1) see indic. refs.]

C̄ in cold and in diffused light adds Cl_2 yielding (2) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179–180° (2). — C̄ adds Br_2 readily yielding (2) 1,1,1-trichloro-2,3-dibromopropane [Beil. I-112], cryst. from alc., m.p. 210° (2)

C̄ with HCl + $FeCl_3$ at 50° for 50–100 hrs. gives (20% yield (3)) 1,1,1,2-tetrachloropropane (3:5785). — [For study of addn. to C̄ of HBr see (3).]

3:5345 (1) Henry, *Bull acad roy Belg.* **1905**, 101–121; *Cent.* **1905**, I 1697. (2) Victoria, *Rec. trav. chim* **24**, 280–283 (1905). (3) Kharasch, Rossin, Fields, *J. Am. Chem. Soc.* **63**, 2558–2560 (1941) (4) Standard Oil Development Co , French 790,852, Nov. 28, 1935, *Cent.* **1936**, I 2672, *C.A.* **30**, 3223 (1936). (5) Henry, *Rec. trav. chim.* **24**, 336–344 (1905).

3:5350 3,4-DICHLOROBUTENE-1 $C_4H_6Cl_2$ **Beil. S.N. 12**
(1,2-Dichlorobutene-3)



B.P. 115° (1)	$n_D^{30.5}$ = **1.4550** (1)
45–45.5° at 40 mm. (1)	

[For prepn. of C̄ (together with other products) from butadiene-1,3 with Cl_2, either directly or in $CHCl_3$, CS_2 or lgr. soln., see (1) (2), the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of C̄ and 1,4-dichlorobutene-2 (3:5725) in the ratio 2:1 (1) (2).]

C̄ does *not* (1) rearr. to 1,4-dichlorobutene-2 (3.5725) even on htg at 90° in a s.t. — However, C̄ in the presence of a metal halide cat. (3) such as $AlCl_3$ (4) rearr. by allylic transposition to 1,4-dichlorobutene-2.

C̄ on htg. at 90° with 2 pts. solid KOH loses HCl yielding (1) (2) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1) (2); under certain conditions, however, C̄ with KOH loses HCl to yield (5) 2-chlorobutadiene-1,3 (chloroprene) (3:7080).

C̄ on htg. in alc. with Zn dust yields (1) butadiene-1,3.

C̄ with Cl_2 yields *solely* (1) the *liq.* isomer of 1,2,3,4-tetrachlorobutane (3:9082).

C̄ treated directly with O_3 at 0°, then with aq., yields (1) α,β-dichloropropionaldehyde (3:9034), b.p. 73° at 50 mm. (1), + formaldehyde (1:0145). — C̄ on oxidn. with dil. alc. $KMnO_4$ gives (1) α,β-dichloropropionic acid (3:0555), m.p. 50° (1).

3:5350 (1) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4043–4055 (1930). (2) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; *Cent.* **1936**, II 3358; *C.A.* **30**, 3912 (1936). (3) I.G. Farbenindustrie, Brit. 505,573, May 12, 1939, *Cent* **1939**, II 1572, *C.A* **33**, 7822 (1939). (4) Nicodemus (to I.G.), U.S. 2,242,084, May 13, 1941; *C.A.* **35**, 5131 (1941). (5) Carothers (to du Pont), U.S. 2,038,538, Apr. 28, 1936; *Cent.* **1936**, II 3358; *C.A.* **30**, 3838 (1936).

3:5356 CHLOROMETHYL ACETATE $CH_3.CO.O.CH_2Cl$ $C_3H_5O_2Cl$ Beil. II - 152
II_1—
II_2-(166)

B.P. 115–116°	at 757 mm.	(1)	$D^{14.3}_{14.3}$ = 1.1953 (1) (13)
115°	at 757 mm.	(13)	
115°		(5)	
113–115°		(2) (12)	
110–112°		(3)	
58–62°	at 290 mm.	(4)	

Colorless liq. with penetrating odor. — Insol. cold aq.; sol. alc., ether. — Sol. in cold conc. H_2SO_4 with evoln. of HCl (1) (13).

[For prepn. of $\bar{C}$ from methyl acetate (1:3005) with Cl_2 in cold (1) (5) and in sunlight (2) (6), or with SO_2Cl_2 in sunlight (6), see indic. refs.; from polyoxymethylene with AcCl (3:7065) in s.t. at 100° (6) or by htg. in pres. of $ZnCl_2$ (61% yield on AcCl (4)) cf. (7) (8) (note that crude $\bar{C}$ may be more or less contaminated with *bis*-(chloromethyl ether) (3:5245), b.p. 105°, and Ac_2O (1:1015), b.p. 140°, apparently produced by disproportionation of $\bar{C}$ itself during the htg. (7).]

$\bar{C}$ on slight warming with aq. readily dissolves by virtue of hydrolysis, yielding (1) (5) (3) formaldehyde (1:0145), AcOH (1:1010), and HCl.

[$\bar{C}$ with alcs. or Na alcoholates (10) presumably first yields alkoxymethylacetates: e g., $\bar{C}$ with Na benzylate in C_6H_6 refluxed for 4 hrs. gives (15% yield (4)) benzyloxymethyl acetate, b.p. 152–155° at 29 mm. (4); however, the usual type of prod. consists of a mixture of formaldehyde dialkylacetal and alkyl acetate (perhaps formed by interchange of radicals between the initial product and the alcohol (9)): e.g., $\bar{C}$ with benzyl alc. (1:6480) gives (9) (10) (13) formaldehyde dibenzylacetal, b.p. 188–190° at 13 mm., + benzyl acetate (1:3751), b.p. 217°; $\bar{C}$ with *n*-propyl alc. (1:6150) gives (9) (13) formaldehyde di-*n*-propylacetal [Beil. I-575, I_1-(301), I_2-(639)], b.p. 137° at 760 mm., + *n*-propyl acetate (1:3075), b.p. 101.6°; for analogous behavior of $\bar{C}$ with MeOH (1:6120) and EtOH (1:6130) see (10).]

[$\bar{C}$ with Na phenolate does *not* yield phenoxymethyl acetate but instead (45% yield (11)) phenyl acetate (1:3571); this may be accounted for in a fashion completely analogous to that suggested above in the case of alcs., but no attempt was made (11) to verify the pres. of formaldehyde diphenylacetal (diphenoxymethane) although the latter [Beil. VI-150] is well known.]

$\bar{C}$ with NH_3 in dry ether gives (12) (13) acetamide, NH_4Cl + formaldehyde (often in the form of hexamethylenetetramine (13)). — $\bar{C}$ with aniline (1.5 moles) in dry ether gives (80% yield (12)) acetanilide, m.p. 114–115°, + 1,3,5-triphenyltrimethylenetriamine ("anhydroformaldehydeaniline") [Beil. XXVI-3], yel. pr., m.p. 140–141° (produced by actn. of the liberated formaldehyde upon the excess of aniline). — [$\bar{C}$ (1 mole) with *N,N*-dimethylaniline (2 moles) + $ZnCl_2$ at 110–120° gives (5) salt of 4,4'-*bis*-(dimethylamino)-diphenylmethane [Beil. XIII-239, $XIII_1$-(71)], m.p. 91°.]

$\bar{C}$ with pyridine forms an unstable addn. cpd. (12); $\bar{C}$ with quinoline forms (12) an addn. cpd., m.p. 214–216° dec., eas. sol. in abs. alc. but easily pptd. with dry ether (12).

[$\bar{C}$ with *N*-potassiopyrrole in dry ether gives (18% yield (14)) *N*-pyrrylmethyl acetate, b.p. 59–63.5° at 3 mm., D^{20}_4 = 1.0916, n^{20}_D = 1.4907 (14).]

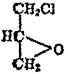
[For study of rate of reactn. of $\bar{C}$ with KI in acetone at 20° and 25° see (2).]

3:5356 (1) Henry, *Ber.* 6, 740–741 (1873). (2) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* 47, 497, 499 (1925). (3) Descude, *Compt. rend.* 132, 1568 (1901). (4) Gupta, Kaushal, Deshapande, *J. Indian Chem. Soc.* 18, 638–640 (1941). (5) Censi, *Bull. soc. ind. Mulhouse* 70, 311–

313 (1899); *Cent.* **1900**, I 594-595. (6) Henry, *Bull. acad. roy. Belg.* **1900**, 48-50, *Cent.* **1900**, I 1122-1123. (7) Descude, *Bull. soc. chim.* (3) **27**, 867-869 (1902); *Compt. rend.* **132**, 1568 (1901). (8) Henry, *Compt. rend.* **133**, 97 (1901). (9) Descude, *Bull. soc. chim.* (3) **27**, 47-48 (1903). (10) Descude, *Bull. soc. chim.* (3) **27**, 1215-1219 (1902).

(11) Kirner, *J. Am. Chem. Soc.* **48**, 2748 (1920). (12) Ulich, Adams, *J. Am. Chem. Soc.* **43**, 663, 665-666 (1921). (13) Descude, *Ann. chim.* (7) **29**, 504-508 (1903). (14) Taggart, Richter, *J. Am. Chem. Soc* **56**, 1386 (1934).

3:5358 3-CHLORO-1,2-EPOXYPROPANE ("Epichlorohydrin"; γ-chloropropylene oxide; (chloromethyl)ethylene oxide)



C_3H_5OCl Beil. XVII - 6, XVII₁-(4)

B.P		
(118-119°		(1) (50))
117°		(2) (3) (4) (5)
116.5-117.5°	at 765 mm.	(6)
116.75-117.00°	at 762.2 mm.	(7)
116.56°	at 760 mm.	(7)
116.5°	at 761 mm	(8)
116.45°	at 760 mm.	(9)
117°	at 758 mm.	(10)
117° cor.	at 755 mm.	(11)
116-118°		(12)
116-117°	at 760 mm.	(13)
116°		(14) (15)
115-117°		(16)
115-116°		(17) (18) (48)
115.4°	at 764 mm.	(19)
115° cor.	at 740 mm.	(20)
		(21)
60-61°	at 100 mm.	(17)
30-32°	at 10 mm.	(22)

M.P. −48° (10)

D_4^{25} = 1.17495 (23)
1.1723 (24)
n_D^{25} = 1.43585 (23)
D_4^{20} = 1.184 (26)
1.1812 (10)
1.181 (17)
1.1801 (25)
1.18 (18)
n_D^{20} = 1.4382 (26)
1.438 (17)
$D_4^{16.1}$ = 1.1848 (25)
$n_D^{16.1}$ = 1.43069 (25)
$D_4^{11.5}$ = 1.1928 (26)
$n_D^{11.5}$ = 1.44195 (26)

C̄ is also sometimes designated as "α-epichlorohydrin" to distinguish it from the less common "β-epichlorohydrin" = β-chlorotrimethylene oxide.

C̄ is liq. with odor suggesting chloroform. — C̄ is spar. sol. aq (see also below) but misc. with alc. or ether.

MISCELLANEOUS PHYSICAL PROPERTIES

Solubility relations. C̄ with aq. forms two layers: the lower layer conts. the following no. of g.'s C̄ per 100 g. satd. soln.: at 25° 98.48 g., at 45° 97.43 g., at 70° 95.82 g., at 80.4° 94.17 g; the upper layer conts. per 100 g. satd. soln.: at 30.2° 6.60 g., at 52.0° 7.53 g., at 65.0° 8.45 g., at 72.0° 9.34 g, at 80.2° 10.43 g. (5).

Binary azeotropes contg. C̄. C̄ with aq. *forms* a homogeneous const. boilg. mixt., b.p. 88°, contg. 75% C̄; at 25° this azeotrope seps. into two layers contg. respectively 98% C̄ and 7% C̄ (17).

[C̄ with AcOH (1:1010) *forms* (9*a*) a *const.-boilg. mixt.*, b.p. 115.05° at 760 mm., contg. 65.5 wt. % C̄; C̄ with tetrachloroethylene (3:5460) forms (9*b*) a const.-boilg. mixt, b.p. 110.12° at 760 mm., contg. 51.5 wt. % C̄.]

[Note that $\bar{C}$ with EtOH (1:6130) (9c) or with formic acid (1:1005) (9d) forms no azeotropes.]

Ternary systems contg. $\bar{C}$. [For extensive study of system $\bar{C}$ + AcOH + aq. see (5).]

MISCELLANEOUS PHYSIOLOGICAL AND BIOCHEMICAL BEHAVIOR OF $\bar{C}$

[For study of toxicity of $\bar{C}$ see (27); for effect on proteins see (28); for effect on wire worms see (29).]

USES OF $\bar{C}$

The uses of $\bar{C}$ both as solvent and as chemical intermediate (see below) are manifold and cannot here be reviewed in detail [however, for use of $\bar{C}$ in stabilization of nitrate esters (30), in refining of mineral oil (31), or in treatment of cellulose fibers to improve dyeing with acid dyes (32) see indic. refs.].

PREPARATION OF $\bar{C}$

[For prepn. of $\bar{C}$ from 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985) with aq. $Ca(OH)_2$ (22) (16) (33), with aq. NaOH (4) (13) (17) (34) (37) cf. (35), with alc. NaOH (36), with ether + NaOH (38), with solid NaOH (39), or with aq. KOH (2) (1) (yields: 95% (33), 92.5% (36), 90% (13) (16) (34), 85% (17), 79% (2), 76–81% (38), 67–72% (22), 70% (17), 60% (4)) see indic. refs.; for patents on prepn. of $\bar{C}$ from this source by use of various alk. materials see (40) (41) (33) (37); note that during this type of prepn. of $\bar{C}$ some glycerol (1:6540) is also formed (38) (44).]

[For prepn. of $\bar{C}$ from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) with aq. alk. see (42) (for studies of kinetics of this loss of HCl see (43)).]

[For formn. of $\bar{C}$ from glycerol (1:6540) with PCl_3 (45), with HCl (1) (50), or S_2Cl_2 (50) see indic. refs.]

[For formn. of $\bar{C}$ from sodium salt of γ-chloro-β-hydroxy-*n*-propyl hydrogen sulfite (itself obtd. from $\bar{C}$ + $NaHSO_3$) on treatment with NaOH see (46).]

[For formn. of $\bar{C}$ from 1-bromo-3-chloropropanol-2 (see below) by loss of HBr by actn. of conc. KOH see (1).]

CHEMICAL BEHAVIOR OF $\bar{C}$ WITH INORGANIC REACTANTS

Reduction of $\bar{C}$. [$\bar{C}$ with Na/Hg in moist ether is very slowly attacked and some allyl alc. (1:6145) (together with other prods.) is formed (47). — Note, however, that reactn. of $\bar{C}$ with Na in ether is very complicated and the prods. and mode of their formn. are disputed (48) (49) (44) (50) (51).] — (For behavior of $\bar{C}$ with HI see below.)

Oxidation of $\bar{C}$. [$\bar{C}$ on oxidn. with HNO_3 ($D = 1.38$) gives (52) β-chloro-α-hydroxypropionic acid (β-chlorolactic acid) [Beil. III-286, III_1-(110), III_2-(209)], eas. sol. aq., alc., ether, cryst. from C_6H_6 (53), m.p. 77° (53), 77–78° (52) (for resolution of this prod. into opt. act. forms, *d*-form, m.p. 91.5°, see (54)). — Note that this prod. is also obtd. by oxidn. of 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038) q.v.]

Halogenation of $\bar{C}$. [$\bar{C}$ with Cl_2 in diffuse light gives (55) γ,γ-dichloropropylene oxide [Beil. XVII-9], oil, b.p. 170°. — $\bar{C}$ with Br_2 at 100° gives (56) (57) *x,x,x*-tribromo-γ-chloropropylene oxide [Beil. XVII-9], oil, which on shaking with aq. forms a crystn. tetrahydrate, m.p. 55° (56).]

Behavior of $\bar{C}$ with water (or dil. acids). [$\bar{C}$ with aq. at 100° (6) in s.t. (1) cf. (60) or on boilg. for 14 hrs. (58) adds H_2O giving (80% yield (58)) 3-chloropropanediol-1,2 (α-

monochlorohydrin) (3:9038). This process is greatly facilitated by the pres. of dil. acids: e.g., for use of dil. H_2SO_4 (yields: 85–90% (34) cf. (59), 80% (36)) or formic acid (66% yield (212)) *see* indic. *refs.*; for study of kinetics of this reactn. incl. influence of various acids and salts see (6) (19) (61) (62); for patent on use of dil. acids or acid-reacting salts see (63). — Note, however, that $\bar{C}$ with aq. contg. 3–20% H_2SO_4 at 100–250° under press. gives (72) acrolein (1·0115).]

Behavior of $\bar{C}$ with halogen hydracids (HX). *With HF.* [$\bar{C}$ with 30% HF soln. reacts vigorously yielding (64a) 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038) and other prods; note that $\bar{C}$ with HF under some circumstances appears to yield (64b) polymers.]

With HCl. [$\bar{C}$ with conc. HCl shaken several hrs. at room temp. (3) (4) cf. (19) (65), or $\bar{C}$ with HCl gas (51) in AcOH (11), gives (80% yield (4)) 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985).]

With HBr. [$\bar{C}$ with const.-boilg. HBr (D = 1.48) as directed (66) cf. (1) gives alm. quant. yield 1-bromo-3-chloropropanol-2 [Beil. I-365, I_1-(185), I_2-(385)], b.p. 197° at 760 mm. (66), 92° at 20 mm. (66), D_4^{20} = 1.726 (67), n_D^{25} = 1.5140 (67) (corresp. *bis-(N-phenylcarbamate)*, m.p. 73° (68))] (See below under reactn. of $\bar{C}$ with metal bromides.)

With HI. [$\bar{C}$ with 66% HI (69) cf. (66) (1) gives 3-chloro-1-iodopropanol-2 [Beil. I-366, I_1-(186), I_2-(386)], b.p. 226° (1), 107° at 19 mm. (66), 110° at 9 mm (69).] (See also below under behavior of $\bar{C}$ with metal iodides.)

Behavior of $\bar{C}$ with oxygenated inorganic acids. [$\bar{C}$ with conc H_2SO_4 (70) or 84% H_2SO_4 in cold (71) gives a corresp mono (acid sulfate) ester [Beil. I-474, I_2-(538)], but whether this HSO_4 group is attached through oxygen to the first or second carbon atoms *of $\bar{C}$ is unknown.*]

[$\bar{C}$ with HNO_3 at not above 20° as directed (73) gives 42% yield of a mononitrate ester of 3-chloropropanediol-1,2 ("α-monochlorohydrin"); $\bar{C}$ with fumg. HNO_3 at 0° gives (74) γ-chloropropylene glycol dinitrate [Beil. I-474]; $\bar{C}$ with mixed $HNO_3 + H_2SO_4$ gives (75) a mixed nitrous/nitric ester [Beil. I-474] of 3-chloropropanediol-1,2 (3·9038).]

[For analogous reactns. of $\bar{C}$ with H_3PO_4 (71) (89) or with $HClO_4$ in ether (76) see indic. refs.; for behavior of $\bar{C}$ toward HOCl see (77).]

Behavior of $\bar{C}$ with salts of inorganic acids. (For behavior with NaCN, etc., see below under *organic reactants.*)

With metal chlorides. [$\bar{C}$ in dry ether adds anhydrous $ZnCl_2$ giving (78) $ClCH_2CH(OZnCl).CH_2Cl$; $\bar{C}$ in dry ether adds anhydrous $MgCl_2$ giving (78) $ClCH_2CH(OMgCl)CH_2Cl$; *both these cpds. on hydrolysis yield (78) 1,3-dichloropropanol-2 ("α-dichlorohydrin")* (3:5985). — Note also that $\bar{C}$ (2 g.) with $MgCl_2$ (1 g.) + aq. (2 ml.) + abs. alc. (5 ml.) in s.t. at 125° for 6 hrs. (79) cf. (11) gives $Mg(OH)_2$ + 1,3-dichloropropanol (above); $\bar{C}$ with alc. $FeCl_3$ gives (11) $Fe(OH)_3$ + 1,3-dichloropropanol-2 (above).] (See also below under reactn. of $\bar{C}$ with RMgX cpds.)

With metal bromides. [$\bar{C}$ *(1 mole) with $MgBr_2$ (1 mole) in dry ether gives* (80) *similarly* $ClCH_2CH(OMgBr).CH_2Br$ which on hydrolysis yields (80) 1-bromo-3-chloropropanol-2 (props. given above under reactn of $\bar{C}$ with HBr).] (See also below under reactn. of $\bar{C}$ with RMgX cpds.)

With metal iodides. [$\bar{C}$ with dry KI in s.t. at 100° for several days (1), or $\bar{C}$ with KI (2 moles) in abs. alc. at 80–85° for 11 hrs. (81), or $\bar{C}$ with NaI (1 mole) in acetone refluxed 21 hrs. (82), gives (40% yield (82)) 3-iodo-1,2-epoxypropane ("α-epiiodohydrin") [Beil. XVII-10], b.p. 167° (1), 64° at 24 mm. (82), 62° at 24 mm. (81).]

[$\bar{C}$ with conc. aq. MgI_2 soln. gives alm. quant. *yield* (170) 3-chloro-1-iodopropanol-2 for whose constants see above under behavior of $\bar{C}$ with HI.]

With alkali sulfides. [For patents on behavior of $\bar{C}$ with aq. Na_2S see (83) (84).] (See also below.)

With alkali sulfites. [$\bar{C}$ with $NaHSO_3$ in s.t. at 100° (11) or htd. under reflux (85) (46) (86) or in cold (87) gives sodium salt of 3-chloro-2-hydroxy-*n*-propyl hydrogen sulfite [Beil. I-474, I_2-(538)].]

[$\bar{C}$ (1 mole) with conc. aq. Na_2SO_3 (2 moles) htd. under reflux 1½–2 hrs. (46) or $\bar{C}$ with conc. aq. K_2SO_3 (85) gives corresp. salts of "glycerol disulfonic acid."]

[For behavior of $\bar{C}$ with Na_3PO_4 (15), with Na_2HPO_4 (88), or with Na_3AsO_3 (90) see indic. refs.]

Behavior of $\bar{C}$ with other non-nitrogenous inorganic reactants. [$\bar{C}$ with PCl_3 gives an addition prod. (91) which with aq. regenerates $\bar{C}$ and also forms H_3PO_3. — $\bar{C}$ with PCl_5 yields (1) 1,2,3-trichloropropane (3:5840) + $POCl_3$.]

[$\bar{C}$ with S_2Cl_2 gives (92) 67% 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985) + 33% α,α′-dichloroacetone (3:0563). — $\bar{C}$ with SO_2Cl_2 + $AlCl_3$ in CCl_4 gives (93) β,β′-dichloroisopropyl chlorosulfonate.]

[$\bar{C}$ in alk. soln. treated with H_2S at 0° gives (94) β-chloro-α-hydroxy-*n*-propyl mercaptan, b.p. 60° at 1.3 mm., D_{-}^{20} = 1.2981, n_D^{20} = 1.5257 (94); at 50°, however, further loss of HCl occurs yielding by ring closure (94) β-hydroxytrimethylene sulfide, b.p. 57° at 1.3 mm., D_{-}^{20} = 1.2130, n_D^{20} = 1.5433 (94). — Note, however, that $\bar{C}$ treated directly at 125° with H_2S gives (95) *bis*-(β-chloro-α-hydroxy-*n*-propyl) sulfide, oil, undistillable without decn. even at 2 mm. (95).]

[$\bar{C}$ with $AsCl_3$ gives (96) *tris*-(β,β′-dichloroisopropyl)arsine, b.p. 88–93° at 10 mm., D_4^{10} = 2.145 (96).]

Behavior of $\bar{C}$ with NH_3 and other inorganic nitrogen cpds. [$\bar{C}$ satd. repeatedly with NH_3 gas as directed (97) gives *tris*-(β-chloro-α-hydroxy-*n*-propyl)amine [Beil. IV-291], m.p. 92–93° (corresp. B.HCl, m.p. 173° (97)); note that from the reactn. prod. of $\bar{C}$ with ethyl acetoacetate treatment with excess alc. NH_3 gives (98) 3-chloro-2-(1?)-aminopropanol-1(2?) [Beil. IV-291].]

[$\bar{C}$ in alc. with NH_3 gas or $\bar{C}$ in alc. with $NaNH_2$, or $\bar{C}$ with aq. NH_4OH (11) (99) gives a reactn. prod. of undetermined constitution, useful in productn. (100) of vat dye printing pastes.]

[$\bar{C}$ with hydrazine hydrate at 100° for 30 min. or in alc. under reflux for 5 hrs. gives (101) γ-hydrazinoepihydrin which with $ZnCl_2$ at 100° gives (101) pyrazole [Beil. XXIII-39, $XXIII_1$-(15)], *m.p.* 69.5–70° (101).]

[For behavior of $\bar{C}$ with basic potassium iminodisulfonate, $KN(SO_3K)_2$, leading to dipotassium epihydrin-*N,N*-disulfonate (102) (103), or with basic potassium hydroxylaminedisulfonate, $KON(SO_3K)_2$, leading to dipotassium epihydrinhydroxylamine-*N,N*-disulfonate (104), see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

Behavior of $\bar{C}$ with Hydroxy and Mercapto Compounds

With monohydric alcohols. $\bar{C}$ with alcohols reacts to give by opening of the oxide ring the corresp. primary ethers of 3-chloropropanediol-1,2("α-monochlorohydrin") (3:9038).

[$\bar{C}$ with MeOH (1:6120) in pres. of H_2SO_4 (105) (66) (106) (107), or $\bar{C}$ with MeOH at elev. temp. under press. (108), or $\bar{C}$ with MeOH + BF_3 (109), gives (yields: 88–90% (105), 89% (106), 74.5% (109)) γ-chloro-β-hydroxy-*n*-propyl methyl ether ("chloromethylin") [Beil. I_2-(538)], b.p. 173° at 752 mm. (105), 172° (106), 170.5–171.5° (109), 95° at 20 mm. (106), D_4^{20} = 1.1618 (109), n_D^{20} = 1.4474 (109). — Note, however, that $\bar{C}$ with MeOH in pres. of KOH gives (110) (111) glycerol α,α′-dimethyl ether (β,β′-dimethoxy-isopropyl alc.)

[Beil. I-512, I_1-(590)], b.p. 167–168° at 760 mm., 65.5–66.0° cor. at 9 mm. (113), D_4^{20} = 1.0085 (113), D_4^{25} = 1.012 (111), n_D^{25} = 1.4183 (111), n_D^{20} = 1.4192 (113) (corresp. p-nitrobenzoate, m.p. 43° (112)).]

[C̄ with EtOH (1:6130) in pres. of H_2SO_4 refluxed 6 hrs. (17) or 20 hrs. (106) gives (yields 80% (106), 76% (17)) γ-chloro-β-hydroxy-n-propyl ethyl ether ("chloroethylin") [Beil. I-474, I_1-(538)], b.p. 183–184° (106), 104–106° at 60 mm. (17), 95–100° at 20 mm. (106), D_4^{25} = 1.107 (17), n_D^{25} = 1.442 (17). — Note, however, that C̄ with EtOH + KOH gives (110) glycerol α,α′-diethyl ether (β,β′-diethoxyisopropyl alc.) [Beil I-512], b.p. 191° at 760 mm. (13) (111), 108–109° at 60 mm. (111), 61.5–62.0° cor. at 2 mm. (113), D_4^{25} = 0.952 (111) (13), D_4^{20} = 0.9514 (113), n_D^{25} = 1.419 (111) (13), n_D^{20} = 1.4200 (113).]

[For corresp. behavior of C̄ with n-butyl alc. (1:6180) + H_2SO_4 (106), with isoamyl alc. (1:6200) + H_2SO_4 (106), see indic. refs. — C̄ with dodecanol-1 (lauryl alc.) (1:5900) + $FeCl_3$ in s.t. at 160° for 18 hrs. (39% yield (114)) or with H_2SO_4 (115) gives γ-chloro-β-hydroxy-n-propyl n-dodecyl ether, b.p. 157° at 1 mm. (114), n_D^{25} = 1.4525 (114). — (For attempts to effect analogous reactn. between C̄ and ter-butyl alcohol (1:6140) in pres. of H_2SO_4 and for physical constants on higher members of di(alkoxy)isopropyl alc. series see (113))]

[C̄ with ethylene chlorohydrin (3:5552) + H_2SO_4 gives (70% yield (116)) γ-chloro-β-hydroxy-n-propyl β-chloroethyl ether, b.p. 123–125° at 18 mm. (116).]

With polyhydric alcohols. [C̄ with ethylene glycol (1:6465) + H_2SO_4 gives (56% yield (117)) γ-chloro-β-hydroxy-n-propyl β-hydroxyethyl ether, b.p. 135–139° (117).]

[For presumably analogous behavior of C̄ with glycerol + H_2SO_4 see (118); for behavior of C̄ with cellulose + 50% NaOH see (119).]

With mercaptans. C̄ with mercaptans behaves in general analogously to C̄ with monohydric alcs. + H_2SO_4.

[E g., C̄ with MeSH is unreported. — C̄ with EtSH at 50° for 4 hrs. gives (90% yield (95)) γ-chloro-β-hydroxy-n-propyl ethyl sulfide, b.p. 114–115° at 16 mm.; note, however, that C̄ with EtSH in aq. KOH (i.e., KSEt) reacts differently yielding (95) 1,2-epoxy-n-propyl ethyl sulfide, b.p. 67–68° at 15 mm., D_4^{22} = 1.0196, n_D^{22} = 1.4789. — C̄ with n-PrSH + activated carbon at 90° for 7 hrs. gives (95) γ-chloro-β-hydroxy-n-propyl n-propyl sulfide, b.p. 95° at 4 mm.]

[C̄ (1 mole) with benzyl mercaptan (1 mole) at 130° for 7 hrs. gives (95) γ-chloro-β-hydroxy-n-propyl benzyl sulfide, b.p. 154–156° at 4 mm.; note, however, that C̄ (1 mole) with benzyl mercaptan (2 moles) in alc. NaOH gives (46) bis-(β,β′-dibenzylmercapto)-isopropyl alc., m.p. 59°.]

[C̄ with thiophenol at 130° for 5 hrs. gives (95) γ-chloro-β-hydroxy-n-propyl phenyl sulfide, b.p. 141° at 4 mm.]

With monohydric phenols. C̄ with monohydric phenols reacts to give by opening of the oxide ring the corresp. primary aryl ethers of 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038).

[C̄ with phenol (1:1420) (2 moles) at 110° for 10 hrs. (17), or at 150–160° under press. (120) (121) cf (122), gives (86% yield (17)) γ-chloro-β-hydroxy-n-propyl phenyl ether ("α-monochlorohydrin γ-phenyl ether") [Beil. VI-147, VI_1-(85)], b.p. 155–156° at 16 mm. (123), 152–153° at 12 mm. (121), 125–126° at 2 mm. (17), D_4^{25} = 1.209 (17), n_D^{25} = 1.540 (17) (this prod. is also formed even in pres. of a very little NaOH (123)). — C̄ (1 mole) with phenol (1:1420) (1 mole) + aq NaOH (1¼ moles) at ord. temp. for 24 hrs. gives (40% yield (17) (125)) (124) 3-phenoxy-1,2-epoxypropane (glycidol phenyl ether) [Beil. XVII-105, $XVII_1$-(50)], b.p. 243–244° cor. (124), 133° at 23 mm. (121), 115–116° at 3–4 mm. (17), D_4^{25} = 1.10 (17), this reactn. occurs so readily that this prod. has formerly been mistaken for glycerol α,γ-diphenyl ether (see following). — C̄ with phenol (1:1420) +

alc. NaOEt under reflux (120) cf. (124) (127) yields glycerol α,α'-di(phenyl) ether (β,β'-diphenoxyisopropyl alc.) [Beil. VI-149, VI_1-(86)], lfts. from alc., m.p. 82° (120) (127), 81–82° (124), 80–81° (17).]

C̄ (1 mole) with *p*-nitrophenol (1 mole) + aq. NaOH (1½ moles) at ord. temp. for some days gives (126) 3-(*p*-nitrophenoxy)-1,2-epoxypropane (glycidol *p*-nitrophenyl ether) [Beil. $XVII_1$-(51)], m.p. 67° cor. (126), 69° (127). — C̄ (1 mole) with 2,4-dinitrophenol (1 mole) in aq. KOH (1 mole) refluxed several days, or C̄ with Ag 2,4-dinitrophenolate in alc., gives (42–47% yield) (note that C̄ is in excess (128)) glycerol α,α'-*bis*-(2,4-dinitrophenyl)ether, m.p. 79° (128).]

[C̄ (1 mole) with *o*-cresol (1:1400) (1 mole) + very dil. aq. NaOH at ord. temp. 9 days gives (30% yield (123)) γ-chloro-β-hydroxy-*n*-propyl *o*-tolyl ether ("α-monochlorohydrin γ-(*o*-tolyl) ether) [Beil. VI_1-(201)], oil, b.p. 165° at 14 mm. (corresp. *N*-phenylcarbamate, m.p. 113–114°); C̄ (1 mole) with *o*-cresol (1 mole) + excess aq. NaOH at ord. temp. 4 days gives (131) 3-(*o*-toloxy)-1,2-epoxypropane (glycidol *o*-cresyl ether) [Beil. XVII-105], oil, b.p. 134.5° at 14 mm. (131); note, however, that C̄ (1 mole) with Na *o*-cresolate (2 moles) in alc. refluxed 24 hrs. gives (37% yield (129)) cf. (130) glycerol α,α'-*bis*-(*o*-tolyl)ether [Beil. VI-354], m.p. 36–37°, b.p. 226° at 13 mm. (129) (130). — C̄ (1 mole) with *m*-cresol (1:1730) (1 mole) + 20% aq. NaOH (1/40 mole) at ord. temp. for 56 days gives (67.5% yield (126)) γ-chloro-β-hydroxy-*n*-propyl *m*-tolyl ether ("α-monochlorohydrin" γ-(*m*-tolyl) ether) [Beil. VI_1-(186)], b.p. 167.5° cor. at 13 mm. (corresp. *N*-phenylcarbamate, m.p. 108–108.5° cor.); C̄ (1 mole) with *m*-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (126) 3-(*m*-toloxy)-1,2-epoxypropane (glycidol *m*-tolyl ether) [Beil. $XVII_1$-(51)], b.p. 139.5–140° cor. at 15 mm.; note, however, that C̄ (1 mole) with Na *m*-cresolate (2 moles) in alc. refluxed several days gives (23% yield (129)) (130) glycerol α,α'-*bis*-(*m*-tolyl) ether [Beil. VI-378], b.p. 232° at 13 mm. (129) (130). — C̄ (1 mole) with *p*-cresol (1:1410 (1 mole) + 20% aq. NaOH (1/20 mole) at ord. temp. for 8 days gives (47% yield (123)) γ-chloro-β-hydroxy-*n*-propyl *p*-tolyl ether ("α-monochlorohydrin" γ-(*p*-tolyl) ether) [Beil. VI_1-(201)], oil, b.p. 165° at 14 mm. (corresp. *N*-phenylcarbamate, m.p. 113–114°); C̄ (1 mole) with *p*-cresol (1 mole) + excess aq. NaOH at ord. temp. gives (124) cf. (120) 3-(*p*-toloxy)-1,2-epoxypropane, (glycidol *p*-cresyl ether) [Beil. XVII-105, $XVII_1$-(51)], b.p. 136° at 17 mm. (124); note, however, that C̄ (1 mole) with Na *p*-cresolate in alc. under reflux gives (120) (124) glycerol α,α'-*bis*-(*p*-tolyl) ether [Beil. VI-395], m.p. 88° (120) (124).]

[The analogous behavior of C̄ with other monohydric phenols cannot be detailed here; however, for C̄ with α-naphthol (1:1500) (120) (126) (132), β-naphthol (1:1540) (126) (127) (132), carvacrol (1:1760) (126), thymol (1:1430) (126), guaiacol (1:1405) (126) (127) see indic. refs.]

With dihydric phenols. [C̄ (1 mole) with pyrocatechol (1:1520) (1 mole) + KOH (1 mole) condenses with ring closure yielding (133) (134) 5-(hydroxymethyl)-2,3-benzodioxane-1,4, m.p. 96°, b.p. 160° at 17 mm. (133) (134).]

[For behavior of C̄ with 4-acetylresorcinol (resacetophenone) see (135).]

Behavior of C̄ with Ethers

[C̄ with dimethyl ether + BF_3 at −35° after reactn. and distn. gives (86.6% yield (136)) *tris*-(β-chloro-β'-methoxy-isopropyl) borate, accompanied by a little γ-chloro-β-hydroxy-*n*-propyl methyl ether (for constants see above under behavior of C̄ with monohydric alcs.). — C̄ with diethyl ether + BF_3 at 20–25° overnight followed by treatment with aq. 2*N* Na_2CO_3 gives mainly (136) γ-chloro-β-hydroxy-*n*-propyl ethyl ether (for constants see above under behavior of C̄ with monohydric alcs.) accompanied by ethyl alcohol (1:6130); direct distillation of the reaction mixt. without Na_2CO_3 treatment, however,

gives (136) *tris*-(β-chloro-β-ethoxyisopropyl) borate, b.p. 210–216° at 12 mm., D_4^{22} = 1.148 (126).]

[C̄ with α-halogen-methyl alkyl ethers in pres. of $HgCl_2$ gives (137) (105) (by ring opening and addn.) mixed formals; e.g., C̄ with chloromethyl methyl ether (3:7085) + $HgCl_2$ gives formaldehyde β,β'-dichloroisopropyl methyl acetal, etc.]

Behavior of C̄ with Carbonyl Compounds

With aldehydes. [C̄ with aldehydes condenses to yield the corresp. 2-alkyl-4-(chloromethyl)-1,3-dioxolanes; (however, the prod. to be expected from C̄ with formaldehyde (1:0145), viz., 4-(chloromethyl)-1,3-dioxolane [Beil. XIX-8, XIX_1-(610)], b.p. 126° at 750 mm. (138), has not been so reported, but rather from 3-chloropropanediol-1,2 ("α-monochlorohydrin")(3:9038)); for behavior of this prod. with solid KOH at 110° involving loss of HCl and formn. (94% yield (139)) (140) of the formal of propen-1-diol-2,3, b.p. 93–95° at 758 mm. (139), n_D^{20} = 1.4336 (139), see indic. refs.]

[C̄ with acetaldehyde (1:0100) + $SnCl_4$ in CCl_4 at 18–25° gives (45% yield (141)) *4-(chloromethyl)-2-methyl-1,3-dioxolane* ("acetaldehyde γ-chloropropylene acetal") [Beil. XIX_1-(610)], b.p. 158–162° at 760 mm. (141). — C̄ with propionaldehyde (1:0110) + $SnCl_4$ in CCl_4 gives (64% yield (141)) (142) 4-(chloromethyl)-2-ethyl-1,3-dioxolane, b.p. 65–70° at 18 mm. (142). — For analogous reactions of C̄ with *n*-butyraldehyde, octanal-1, decanal-1, and dodecanal-1 see (142); with crotonaldehyde see (141).]

With ketones. C̄ with ketones condenses in completely analogous fashion to yield the corresp. 2,2-dialkyl-1,3-dioxolanes. [E.g., C̄ (converted to 3-chloropropanediol-1,2 ("α-monochlorohydrin") (3:9038) although this may be unnecessary) gives (60% yield (58)) 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane ("acetone-glycerol α-chlorohydrin"), b.p. 157° at 767 mm., D_4^{20} = 1.1079, n_D^{15} = 1.43750 (58). — C̄ with benzophenone (1:5150) + $SnCl_4$ in CCl_4 at 13–25° gives (73% yield (141)) 4-(chloromethyl)-2,2-diphenyl-1,3-dioxolane, m.p. 44.5°, b.p. 159–167° at 2–3 mm. (141). — For analogous behavior of C̄ with phenacyl bromide, camphor, and cyclopentadecanone see (141).]

Behavior of C̄ with Organic Acids

(For salts, acid chlorides, acid anhydrides, see below.)

With aliphatic monobasic acids. [C̄ with AcOH (1:1010) in s.t. at 180° for 24 hrs. (143) cf. (1) gives a mixt. of both glycerol α-chlorohydrin α'-acetate (3:6775) and glycerol α-chlorohydrin β-acetate (3:6517); C̄ with AcOH + a little $FeCl_3$ at room temp. for 24 hrs. gives (90% yield (144)) a prod. supposed originally (144) to be glycerol α-chlorohydrin α'-acetate (3:6775); note, however, that later workers (36) could obtain only 25% yield unless mixt. stood 15 days at room temp. or 2 days at 80° and regarded the product as glycerol α-chlorohydrin β-acetate (3:6517). — C̄ with aliphatic monobasic acids contg. at least 4 carbon atoms + $AlCl_3$ (145) or C̄ with aliphatic, alicyclic, or aromatic acids (contg. no sulfonic acid groups) + pyridine (146) gives corresp. mono esters (probably mixt. of α- and β-) of 3-chloropropanediol-1,2 (3:9038).]

[C̄ with trichloroacetic acid (3:1150) undergoes ring closure (similar to that of C̄ with carbonyl cpds. above) giving (147) 4-(chloromethyl)-2-hydroxy-2-(trichloromethyl)-1,3-dioxolane, b.p. 99–101° at 0.11 mm., n_D^{23} = 1.4892.]

[C̄ with thiolacetic acid ($CH_3.CO.SH$) at 60° for 12 hrs. gives (76% yield (148)) γ-chloro-β-hydroxy-*n*-propyl thiolacetate, b.p. 100–101° at 1 mm., D_{-}^{20} = 1.2806, n_D^{20} = 1.5186; on longer htg., e.g., 35 hrs. at 60°, *or even at ord. temp.* on 2 weeks stgd. in diffuse light, largely rearr. to β-chloro-β'-mercapto-isopropyl acetate, b.p. 69–70° at 1 mm., D_{-}^{20} = 1.2308, n_D^{20} = 1.4855 (148).]

With HCN (or its salts). [C̄ with excess anhydrous HCN in s.t. at 75–85° for 90 hrs. (149) (150) cf. (151) (152), or C̄ with anhydrous HCN + some solid KCN in s.t. at ord. temp. for 3–4 days (153), or C̄ with aq. $Ca(CN)_2$ (154), gives (yields: 85% (153), 72% (150), 70% (151), 65% (149)) γ-chloro-β-hydroxy-n-butyronitrile [Beil. III-310], b.p. 250° dec. (151), 140° at 20 mm. (151), 134–135° at 15 mm. (153), 110–111° at 2 mm. (151), D_{-}^{15} = 1.233 (153), n_D^{15} = 1.4735 (153). — Note, however, that C̄ with aq. or alc. KCN splits out KCl giving (155) (85) 3-cyano-1,2-epoxypropane ("epicyanhydrin") [Beil. XVIII-261], m.p. 162°.]

Behavior of C̄ with Salts of Organic Acids

[C̄ with dry KOAc first at 110°, later at 150° (156) cf. (157), or at 120–135°, later 150° (18) (158), gives 3-acetoxy-1,2-epoxypropane (glycidyl acetate) [Beil. XVII-106], b.p. 168–169° (157), 167–168° (143), 162–164° at 750 mm. (158), accompanied by other prods. (for study of polymerization of this prod. see (18) (158)).]

C̄ with aq. K cyanate on boilg. (159) (160) or C̄ with free isocyanic acid (from htg. cyanuric acid) in cold (160) adds yielding 5-(chloromethyl)oxazolidone-2 [Beil. XXVII-145, $XXVII_1$-(260)], pr. from aq., C_6H_6, or Ac_2O, m.p. 106° (161) (159), 105° (159).

[For behavior of C̄ with disodium methyl phosphate (162) or with disodium glycerophosphate (163) see indic. refs.]

Behavior of C̄ with Acid Chlorides

C̄ with acid chlorides yields corresp. esters of β,β′-dichloroisopropyl alc. ("glycerol α-dichlorohydrin") (3:5985) as exemplified by the following illustrations.

With aliphatic acid chlorides. [C̄ with AcCl (3:7065) (164) in s.t. at 100° for 2 hrs. (165) or 30 hrs. (166) gives (73% yield (164)) *β,β′-dichloroisopropylacetate (3:6318)*. — C̄ with propionyl chloride (3:7170) in s.t. at 135° for 3 hrs. gives (167) β,β′-dichloroisopropyl propionate [Beil. II_2-(221)], b.p. 208°, D_{20}^{20} = 1.2222 (167). — C̄ with n-butyryl chloride (3:7370) in s.t. at 100° (166) or with exclusion of aq. in flask at 75° for 8 hrs. (167) gives β,β′-dichloroisopropyl n-butyrate [Beil II-271, II_2-(246)], b.p. 226–227° at 738 mm. (166), 223.5° (167), D_{20}^{20} = 1.1792 (167), n_D^{20} = 1.4540 (167). — C̄ with isovaleryl chloride (3:7560) gives (166) (168) β,β′-dichloroisopropyl isovalerate [Beil. II-312, II_2-(275)], b.p. 245° at 737 mm. (166), 127–140° at 36 mm. (168), D_{-}^{20} = 1.444 (168), n_D^{20} = 1.450 (168). — C̄ with stearoyl chloride (3.9960) in s.t. at 130° for 3½ hrs. gives (167) β,β′-dichloroisopropyl stearate [Beil. II_2-(352)], m.p. 39.5°.]

Behavior of C̄ with Acid Anhydrides

With anhydrides of aliphatic acids. [C̄ with Ac_2O (1:1015) in s.t. at 180° for 4 hrs. (166) or C̄ with Ac_2O + $FeCl_3$ at ord. temp. for 24 hrs. (144) gives (90% yield (144)) β,β′-dichloroisopropyl acetate (3:6318).]

With anhydrides of aromatic acids. [C̄ with phthalic anhydride (1:0725) + dimethylaniline at 100° is claimed (169) to give the monomolecular neutral phthalate [Beil. XIX-165] of 3-chloropropanediol-1,2.]

Behavior of C̄ with Organometallic Compounds (or Their Equivalents)

Behavior with Grignard compounds. *With RMgX cpds. from alkyl or alkaryl halides* [C̄ with MeMgI in dry ether evolves gas (CH_4?) and after acidification yields (171) 3-chloro-1-iodopropanol-2 (for constants see above under behavior of C̄ with HI).]

[The reactn. of C̄ with EtMgBr may give three different prods. (or mixtures of them) according to circumstances: the first of these is 1-bromo-3-chloropropanol-2 (for constants

see above under behavior of $\bar{C}$ with HBr); the second is the expected 1-chloropentanol-2 (3:8225); the third is cyclopropanol, b.p. 100–103° (80) (172), $D_{20}^{20} = 0.9110$ (80), $n_D^{20} = 1.4129$ (80) (corresp. p-nitrobenzoate, m.p. 72.0–72.5°; 3,5-dinitrobenzoate, m.p. 108–109°; *N*-phenylcarbamate, m.p. 101.5–102.0°; *N*-(p-nitrophenyl)carbamate, m.p. 159–160°; *N*-(α-naphthyl)carbamate, m.p. 100.5–101.5° (172)). — Note that $\bar{C}$ with EtMgBr gives (16–19% yield (67) (173)) 1-chloropentanol-2 (3:8225), while $\bar{C}$ with $MgEt_2$ gives 70–83% yield (80). — For review of earlier work on this rather complex system see (80) (173) (67).]

[For behavior of $\bar{C}$ with 15 other RMgX cpds. leading in general to chlorohydrins of type $RCH_2CH(OH)CH_2Cl$ see (173).]

With RMgX cpds. from aryl halides. [$\bar{C}$ with C_6H_5MgBr gives (18% yield (173)) (132) (174) (175) 3-chloro-1-phenyl-propanol-2 [Beil. VI-503], b.p. 254–257° (174), 153–154° at 28 mm. (174) (175), 142–144° at 23 mm. (173), $D_{25}^{25} = 1.1528$ (173), $n_D^{25} = 1.5470$ (173) (corresp. 3,5-dinitrobenzoate, m.p. 120–121° (173)). — For analogous behavior of $\bar{C}$ with RMgX cpds. from α-bromonaphthalene and from *p*-bromanisole (*p*-bromophenyl methyl ether) see (132).]

Behavior with various sodio derivatives. [$\bar{C}$ with diethyl sodiomalonate in abs. alc. at 50° does *not* split out NaCl but rather by ring opening, addn. of reactant, and elimination of EtOH ppts. (176) (177) cf. (178) the monosodium enolate (m.p. 172° dec. (176)) of *α-carbethoxy-δ-chloro-n-valero-γ-lactone* [Beil. XVIII-373, $XVIII_1$-(478)], set free (yields: 78% (177), 50% (176)) by acidification as an oil, b.p. 180–182° at 12 mm. (176), 175–180° at 12 mm. (177). — Note that this lactone with excess alc. NH_3 gives on evapn. (176) (179) γ-chloro-β-hydroxy-*n*-propylmalondiamide [Beil. III-450], m.p. 117–118°.]

[$\bar{C}$ with ethyl sodioacetoacetate in abs. alc. at 50° does *not* split out NaCl but rather by ring opening, etc., as in preceding case gives after acidification (yields: 80% (176), 74% (177)) *α-aceto-δ-chloro-n-valero-γ-lactone* [Beil. XVII-421, $XVII_1$-(230)], b.p. 168° at 16 mm. (177), 163° at 12 mm. (176).]

[$\bar{C}$ with ethyl sodio-benzoylacetate in abs. alc. behaves in analogous fashion yielding after acidification (180) *α-benzoyl-δ-chloro-n-valero-γ-lactone* [Beil. XVII-497], m.p. 103–106°.]

Behavior of $\bar{C}$ with Amines

With primary amines. *With aliphatic primary amines.* This reactn. appears not to to have been thoroughly studied [however, for reactn. of $\bar{C}$ with $MeNH_2$ (181) and use of prod. in prepn. of vat dye printing pastes (182) see indic. refs.].

With alicyclic primary amines. [$\bar{C}$ (1 mole) with cyclohexylamine (3½ moles) under reflux gives (18% yield (82)) *β,β′-bis*-(cyclohexylamino)isopropyl alc., m.p. 72–73°.]

With aromatic primary amines. [$\bar{C}$ (1 mole) with aniline (2 moles) in toluene refluxed 95 hrs. gives (yield not stated (71)) 3-(phenylamino)-1,2-epoxypropane ("glycidanilide"). — $\bar{C}$ (1 mole) with aniline (3 moles) at 140° is claimed (183) to yield *β,β′-bis*-(phenylamino)isopropyl alc. [Beil. XII-553], m.p. 53–54°, but later workers could obtain only viscid oils (181) or a further reactn. prod. supposed (185) to be *β*-(phenylamino)-*β′*-(diphenylamino)isopropyl alc., m.p. 350° dec. (185).]

[$\bar{C}$ (1 mole) with *p*-toluidine (2 moles) might be expected to yield 3-(*p*-tolylamino)-1,2-epoxypropane, but no such cpd. appears to have been recorded. — However, $\bar{C}$ (1 mole) with *p-toluidine (1 mole) in dil. alc.* (186) (184) (82) (but *not* in C_6H_6 (184)) opens ring to yield by addn. *β*-chloro-*β′*-(*p*-tolylamino)isopropyl alc., m.p. 85° (184), 81–82° (186); this prod. on htg. with *p*-toluidine (184) or $\bar{C}$ (1 mole) with *p*-toluidine (2 moles) at 155° (186) gives *β,β′-bis*-(*p*-tolylamino)isopropyl alc., m.p. 116° (184), 113.5° (186).]

[$\bar{C}$ with *p*-phenetidine hydrochloride in aq. soln. at ord. temp. especially in sunlight gives (40% yield (187)) cf. (188) *N,N-bis*-(γ-chloro-β-hydroxy-*n*-propyl)phenetidine.]

[For behavior of C̄ with β-naphthylamine in xylene under reflux (189), with arsanilic acid (190), or with p-aminophenol (or its ethers) (191) see indic. refs.]

With heterocyclic primary amines. [C̄ with α-aminopyridine gives (63% yield (192)) by addn. to oxide ring and subsequent ring closure a prod., m.p. 190°, regarded as "1,2-divinylene-5-hydroxytetrahydropyrimidine."]

With phenylhydrazine. [C̄ with 1½ pts. phenylhydrazine in ether at not above 15° for 10 days ppts. phenylhydrazine hydrochloride and leaves in the other 4-hydroxy-1-phenylpyrazolidine [Beil. XXIII-348], m.p. 103–104° (193); this prod. with phenylhydrazine hydrochloride on warming in C_6H_6 (193) or C̄ with 2 pts. phenylhydrazine in C_6H_6 refluxed 8–9 hrs. (194) gives (58% yield (194)) 1-phenylpyrazole (Beil. XXIII-40, XXIII$_1$-(15)], b.p. 246.5° cor. at 765.4 mm. (194), m.p. 11–11.5° (194), D_4^{20} = 1.1127 (195), n_D^{20} = 1.5966 (195).]

With secondary amines. *With aliphatic secondary amines.* [C̄ with Me_2NH presumably gives (196) β-chloro-β′-(dimethylamino)isopropyl alc., but no constants are reported in the literature, either for it or for its ring-closure derivative, 3-(dimethylamino)-1,2-epoxypropane, cf. (196); note further that the prod. to be expected from C̄ + 2 Me_2NH, viz., β,β′-*bis*-(dimethylamino)isopropyl alc. [Beil. IV-290] (197), although known, has not been prepd. from C̄, but only by other means.]

[C̄ with aq. Et_2NH gives (196) (198) cf. (199) 3-(diethylamino)-1,2-epoxypropane [Beil. XVIII-583], b.p. 155–159 at 760 mm. (198), 55–60° at 15 mm. (196), 40–50° at 8 mm. (198), D_4^{15} = 0.8876 (196). — C̄ (1 vol.) with Et_2NH (3½ vols.) refluxed 2–3 hrs. gives (82% yield (200)) β,β′-*bis*-(diethylamino)isopropyl alc., b.p. 114° at 9 mm. (corresp. B̄.2PkOH, m.p. 163° (200).]

[C̄ with di-n-propylamine (2 moles) gives (70% yield (215)) 1,3-*bis*-(di-n-propylamino)-propanol-2, b.p. 99–101° at 3 mm., D_4^{20} = 0.8624, n_D^{20} = 1.4483 (215).]

With aromatic secondary amines. [C̄ with N-methylaniline gives (198) cf. (199) 3-(N-methylanilino)-1,2-epoxypropane, b.p. 160–162° at 30 mm. (198), 132–135° at 8 mm. (198); note, however, that C̄ (1 mole) with N-methylaniline (1 mole) at 100° for 4 hrs. (82) gave none of the preceding cpd. but a very small yield (2%) of β,β′-*bis*-(N-methylanilino)isopropyl alc., m.p. 82°, accompanied by other prods.]

[C̄ with diphenylamine at 160–170° under press. splits out HCl and ring-closes with loss of H_2O yielding (201) 1-phenyl-3-hydroxy-1,2,3,4-tetrahydroquinoline [Beil. XXI$_1$-(205)], m.p. 79°, b.p. 200° at 5 mm.]

With heterocyclic secondary amines. [C̄ with piperidine gives (196) (198) by elimination of HCl 3-(piperidino)-1,2-epoxypropane, b.p. 86.5–88° at 15 mm. (196), 72–77° at 8 mm. (198), D_4^{16} = 0.9669 (196).]

With tertiary amines. C̄ with tertiary amines gives quaternary salts, but this reactn. is often followed by opening of the oxide ring and addn. of reactant.

With aliphatic tertiary amines. [C̄ with alc. Et_3N (1 mole) in s.t. at 100° gives (202) a little of the corresp. quat. salt, viz., triethyl-(β,γ-epoxy-n-propyl)ammonium chloride [Beil. XVIII-583]; note, however, that C̄ with alc. Et_3N (1 mole) in s.t. at 100° for 6 hrs. gives also (202) (203) 2-hydroxytrimethylene-1,3-*bis*-(triethyl-ammonium chloride) [Beil. IV-290] together with other prods.]

[For behavior of C̄ with N,N-dimethyl-"stenyl" amine see (204).]

With heterocyclic tertiary amines. [For study of behavior of C̄ with pyridine see (205) (206); with quinoline see (207).]

Behavior of C̄ with Other Nitrogenous Reactants

(Note that in the following examples reaction occurs by opening of the oxide ring and that elimination of chlorine, if it occurs at all, is effected only in a subsequent ring closure.)

[C̄ (1 mole) with disodium cyanamide (1 mole) in aq. soln. at ord. temp. for 24 hrs. presumably first yields the sodium deriv. of *N*-(γ-chloro-β-hydroxy-*n*-propyl)cyanamide, but this immediately ring-closes giving (33% yield (208)) 5-(chloromethyl)-2-amino-oxazoline, m.p. 142°.]

C̄ (1 mole) with *p*-toluenesulfonanilide (1 mole) + a few drops pyridine at 120° reacts vigorously giving (86% yield (209)) *N*-(γ-chloro-β-hydroxy-*n*-propyl)-*N*-phenyl-*p*-toluenesulfonamide, m.p. 96–97°; note that this prod. in boilg. alc. on treatment with NaOH loses HCl and ring-closes (92% yield (209)) to the corresp. *N*-(β,γ-epoxy-*n*-propyl)-*N*-phenyl-*p*-toluenesulfonamide, m.p. 77°.

[C̄ (1 wt. pt.) with phthalimide (1 wt. pt.) at 140–150° for 3 hrs. gives (35% yield on phthalimide (210)) cf. (211) (212) *N*-(γ-chloro-β-hydroxy-*n*-propyl)phthalimide [Beil. XXI₁-(369)], m.p. 95.0–96.5° (210), 96–97° (213). — Note that *N*-[(β,γ-epoxy)-*n*-propyl] phthalimide ("phthalimidoepihydrin"), m.p. 93–94° (213), has been prepd. (75% yield (213)) from 3-bromo-1,2-epoxypropane ("epibromohydrin") with K phthalimide, and in $CHCl_3$ with HCl gas or even directly with conc. HCl opens the oxide ring to give (213) the above *N*-(γ-chloro-β-hydroxy-*n*-propyl)-phthalimide, m.p. 96–97° (213).]

COLOR REACTION OF C̄

Color reaction with pyridine (and pyridine bases). C̄ in MeOH with pyridine and/or various "pyridine bases" gives specific color reactions; these can be used for detection of "pyridine bases," e.g., in denatured alcohol and probably vice versa; for detailed study see (214).

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(71) Zetsche, Aeschlimann, *Helv. Chim. Acta* **9**, 711–714 (1926). (72) Groll, Hearne (to Shell Development Co.), U.S. 2,106,347, Jan. 25, 1938; *Cent.* **1938**, II 1676; *C.A.* **32**, 2542–2543 (1938). (73) I.G., French 846,575, Sept. 20, 1939; *C.A.* **35**, 1071 (1941). (74) Henry, *Ann.* **155**, 166, 168–169 (1870). (75) Henry, *Ber.* **4**, 703 (1871). (76) Hofmann, Zedwitz, Wagner, *Ber.* **42**, 4391 (1909). (77) Carius, *Ann.* **134**, 73–75 (1865). (78) Ribas, Tapia, *Anales soc. españ. fís. quím.* **28**, 636–644 (1930), *Cent.* **1932**, II 3862; *C.A.* **24**, 4265 (1930). (79) Delaby, *Ann. chim.* (9) **20**, 67–68 (1923). (80) Magrane, Cottle, *J. Am. Chem. Soc.* **64**, 484–487 (1942).

(81) Nef, *Ann.* **335**, 237–238 (1904). (82) Wedekind, Bruch, *Ann.* **471**, 78, 94, 95, 97 (1929).

l. **27**, 166 (1933). (87) Lumière,
(88) Bailly, *Bull. soc. chim.* (4) **29**, 274–280 (1921). (89) Cavalier, *Ann. chim.* (7) **18**, 482–483 (1899). (90) Oechslin (to Etab. Poulenc Frères), Brit. 191,028, Feb. 14, 1923; *Cent.* **1923**, IV 721; *C.A.* **17**, 2887 (1923); French 556,366, July 19, 1923; *Cent.* **1923**, IV 721; not in *C.A.*

(91) Hanriot, *Bull. soc. chim.* (2) **22**, 550–552 (1879). (92) Malinovskii, *J. Gen. Chem.* (*U.S.S.R.*)
(1928).
(1939).
(*U.S.S.R*
115–117 (1887); *Ber.* **21**, Referate 646 (1888). (98) Schiff, *Gazz. chim. ital.* **21**, II 1–6 (1891). (99) Stallmann (to du Pont Co.), U.S. 1,977,251, Oct. 16, 1934; *Cent.* **1935**, I 2603; *C.A.* **29**, 352 (1935). (100) Stallman (to du Pont Co.), U.S. 1,977,250, Oct. 16, 1934; *Cent.* **1935**, I 1619; *C.A.* **29**, 352 (1935).
–465 (1890). (102) Traube,
W Dec. 17, 1920; *Cent.* **1921**,
II 0). (105) Blanchard, *Bull. soc. chim.* (4) **39**, 1263–1265 (1926). (106) Fourneau, Ribas, *Bull. soc. chim.* (4) **39**, 1584–1589 (1926). (107) I.G., Brit. 271,169, June 16, 1927; *Cent.* **1927**, II 2110; *C.A.* **22**, 1596 (1928). (108) I.G., French 697,786, Jan 22, 1931; *Cent.* **1931**, I 2394; [*C.A.* **25**, 3013 (1931)]. (109) Petrov, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 1918–1922 (1940); *C.A.* **35**, 3603 (1941). (110) Zunino, *Atti accad. Lincei* (5) **6**, II 348 (1897).

(111) Fairbourne, Gibson, Stephens, *J. Chem. Soc.* **1931**, 450, 454. (112) Fairbourne, *J. Chem. Soc.* **1929**, 1151–1152. (113) Henze, Rogers, *J. Am. Chem. Soc.* **61**, 434–435 (1939). (114) Grummitt, Hall, *J. Am. Chem. Soc.* **66**, 1229 (1944). (115) Henkel et Cie, French 744,749, April 26, 1933; *Cent.* **1933**, II 2210; *C.A.* **27**, 4242 (1933). (116) Fourneau, Ribas, *Bull. soc. chim.* (4) **41**, 1053 (1927). (117) Kharasch, Nudenberg, *J. Org. Chem.* **8**, 189 (1943). (118) Loehr (to I.G.), Ger. 510,422, Oct. 18, 1930; *Cent.* **1931**, I 154; [*C.A.* **25**, 964 (1931)]. (119) Dreyfus,

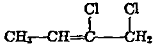
Brit. 166,767, Aug. 18, 1921; *Cent.* **1921**, IV 1140; *C.A.* **16**, 830 (1922). (120) Lindeman, *Ber.* **24**, 2146–2148 (1891).
(121) Fischer, Krämer, *Ber.* **41**, 2730 (1908) (122) Fourneau, *J. pharm. chim.* (7) **1**, 58 (1910); *Cent* **1910**, I 1134; *C.A.* **4**, 3070 (1910). (123) Boyd, Marle, *J. Chem. Soc.* **97**, 1788–1790 (1910). (124) Boyd, Marle, *J. Chem. Soc.* **93**, 839–841 (1908). (125) Böeseken, *Rec. trav chim.* **34**, 102 (1915). (126) Marle, *J. Chem. Soc.* **101**, 305–317 (1912). (127) Fourneau (to Etab. Poulenc Frères), Ger. 228,205, Nov. 7, 1910, *Cent.* **1910**, II 1790–1791, [*C.A.* **28**, 2155 (1911)]. (128) Brenans, *Bull. soc. chim.* (4) **13**, 529–530 (1913). (129) Boyd, *J. Chem. Soc.* **83**, 1137–1138 (1903). (130) Boyd, Marle, *J. Chem. Soc* **95**, 1807–1808 (1909).
(131) Boyd, Knowlton, *J. Chem. Soc.* **95**, 1803 (1909). (132) Fourneau, Trefouel, *Bull. soc. chim.* (4) **43**, 454–458 (1928). (133) Fourneau, Maderin, LeStrange, *J. pharm. chim.* (8) **18**, 185–191 (1933), *Cent.* **1934**, I 391, *C.A.* **27**, 5738 (1933). (134) Soc. Usines Chim. des Rhone-Poulenc, Brit. 420,978, Dec. 20, 1924, *Cent* **1935**, I 2216, [*C.A* **29**, 3468 (1935)]. French 770,485, Sept. 14, 1934, *Cent.* **1935**, I 2216; *C.A.* **29**, 477 (1935). (135) Nadkarni, Wheeler, *J. Chem. Soc.* **1936**, 589–591. (136) Meerwein, Hinz, Hofmann, Kroning, Pfeil, *J. prakt. Chem.* (2) **147**, 258–260, 268–273 (1936/7). (137) Blanchard, *Bull. soc. chim.* (4) **49**, 281–289 (1931). (138) *Bull soc. chim.* (3) **21**, 276–277 (1899). (139) Fischer, Baer, Reldmann, *Ber.* **63**, 1738–1739 (1930). (140) Fischer, Baer, Pollock, Nidecker, *Helv. Chim. Acta* **20**, 1214 (1937).
(141) Willfang, *Ber.* **74**, 145–153 (1941). (142) Bersin, Willfang, *Ber.* **70**, 2167–2173 (1937). (143) Bigot, *Ann. chim.* (6) **22**, 491, 493 (1891). (144) Knoevenagel, *Ann.* **402**, 134–138 (1914). (145) Stein (to General Aniline and Film Corpn.), U.S. 2,224,026, Dec. 3, 1940, *C.A.* **35**, 1802 (1941). Brit. 509,072, Aug 10, 1939, *Cent.* **1939**, II 4351, *C A.* **34**, 2862 (1940). French 850,709, Dec. 23, 1939, *C A.* **36**, 1947 (1942) (146) Stein (to I G), Ger. 708,463, June 12, 1941, *C.A.* **37**, 3105 (1943). French 853,647, March 23, 1940, *C A.* **36**, 2565 (1942). (147) Hibbert, Greig, *Can. J. Research* **4**, 262 (1931). (148) Sjoberg, *Ber.* **74**, 64–65, 69–70 (1941). (149) Braun, *J. Am. Chem. Soc.* **52**, 3170 (1930). (150) Linneweh, *Z physiol. Chem.* **176**, 217 (1928).
(151) Lespieau, *Bull. soc chim.* (3) **33**, 462–463 (1905), *Compt rend.* **127**, 965 (1898), **129**, 225 (1899). (152) Hörmann, *Ber.* **12**, 23–24 (1879) (153) Rambaud, *Bull. soc chim.* (5) **3**, 138–139 (1936). (154) I G , Brit. 348,134, June 4, 1931, *Cent.* **1931**, II 1193; [*C.A.* **26**, 2748 (1932)]: French 702,023, March 27, 1931; *Cent.* **1931**, II 1193; *C A.* **25**, 4012 (1931). (155) Hartenstein, *J. prakt. Chem* (2) **7**, 297–298 (1873). (156) Breslauer, *J. prakt. Chem.* (2) **20**, 188–193 (1879). (157) de Gegerfelt, *Bull soc. chim.* (2) **23**, 160–161 (1871). (158) Levene, Walti, *J. Biol. Chem.* **79**, 363–376 (1928). (159) Thomsen, *Ber.* **11**, 2136–2137 (1878). (160) Paterno, Cingolani, *Gazz. chim ital* **38**, I 243–247 (1908).
(161) Johnson, Guest, *Am Chem. J* **44**, 453, 460 (1910). (162) Bailly, Gaumé, *Compt. rend.* **198**, 1932–1934 (1934). (163) Bailly, Gaumé, *Bull. soc. chim.* (4) **39**, 1420–1428 (1926). (164) Sjöberg, *Svensk Kem. Tid* **53**, 454–457 (1941), *Cent.* **1942**, II 25, *C A.* **37**, 4363 (1943). (165) Abderhalden, Weill, *Fermentforschung* **4**, 84 (1920). (166) Truchot, *Ann* **138**, 297–299 (1866); **140**, 244–246 (1866). (167) Whitby, *J. Chem. Soc.* **1926**, 1460. (168) Humnicki, *Bull. soc. chim* (4) **45**, 281 (1929). (169) Weinschenk, *Chem Ztg* **29**, 1311 (1905). (170) Grignard, *Bull. soc. chim.* (3) **29**, 944, note 2 (1903).
(171) Kling, *Compt. rend* **137**, 756 (1903); *Bull. soc. chim.* (3) **31**, 14–16 (1904) (172) Stahl, Cottle, *J. Am Chem. Soc.* **65**, 1782–1783 (1943). (173) Koelsch, McElvain, *J. Am. Chem. Soc.* **52**, 1164–1169 (1930). (174) Fourneau, Tiffeneau, *Bull. soc chim.* (4) **1**, 1227–1233 (1907). (175) J D Riedel, A G., Ger. 183,361, April 10, 1907, *Cent.* **1907**, I 1607, [*C A.* **1**, 2336 (1907)]. (176) Traube, Lehman, *Ber.* **34**, 1972–1980 (1901). (177) Leuchs, *Ber.* **44**, 1509–1511 (1911). (178) Michael, Weiner, *J. Am. Chem. Soc.* **58**, 1000, 1002 (1936); **56**, 2012–2013 (1934). (179) Traube, Lehman, *Ber.* **32**, 721 (1899). (180) Haller, *Bull. soc. chim.* (3) **31**, 367–369 (1904); (3) **21**, 564 (1899).
(181) Stallmann (to du Pont Co), U S 1,977,253, Oct. 16, 1934; *Cent.* **1935**, I 2603; *C.A.* **29**, 352 (1935). (182) Stallman (to du Pont Co.), U.S. 1,977,252, Oct. 16, 1934; *Cent.* **1935**, I 1620; *C.A.* **29**, 352 (1935). (183) Fauconnier, *Compt. rend.* **106**, 605 (1888); **107**, 250 (1888). (184) Dains, Brewster, Blair, Thompson, *J. Am. Chem. Soc.* **44**, 2641–2642 (1922). (185) Fukagawa, *Ber.* **68**, 1344–1346 (1935). (186) Cohn, Friedländer, *Ber.* **37**, 3034–3035 (1904). (187) Strukov, *Khim. Farm. Prom.* **1934**, No. 2, 11; *Cent.* **1935**, I 2806; *C.A.* **28**, 5421 (1934). (188) Fourneau, Ranedo, *Anales soc. espan fis. quim* (2) **18**, 133–139 (1920); *Cent* **1921**, III 781; *C.A.* **15**, 1885 (1921). (189) Dreyfus, French 702,553, April **11**, 1931; *Cent.* **1931**, II 2058; *C.A.* **25**, 4284 (1931). (190) Lewis (to Parke-Davis Co), U.S. 1,664,123, March 27, 1928; *Cent.* **1929**, I 1047; *C.A.* **22**, 1595 (1928)
(191) Kolsborn, Ger. 346,385, Dec. 29, 1921; *Cent.* **1922**, II 574; not in *C.A.*: Brit. 155,575, 155,576, Jan. 13, 1921, *Cent.* **1921**, II 601–602; *C.A.* **15**, 1535 (1921): French 519,129, June 4, 1921; *Cent.* **1921**, IV 803; not in *C.A.* (192) Knunyantz, *Ber.* **68**, 397–399 (1935): *Compt. rend.*

acad. sci. (*U.R.S.S.*) **1935**, I 501–506; *Cent.* **1936**, II 2915; not in *C.A.* (193) Gerhardt, *Ber.* **24**, 352–357 (1891). (194) Balbiano, *Gazz. chim. ital.* **17**, 177 (1887); **18**, 356–357, 375 (1888); **19**, 128 (1889). (195) Rosanov, *J. Russ. Phys.-Chem. Soc.* **48**, 1227 (1916); *Cent.* **1923**, III 1080; not in *C.A.* (196) Drozdov, Cherntzov, *J. Gen. Chem.* (*U.S.S.R.*) **4**, 969–974 (1934); *Cent.* **1936**, I 42; *C.A.* **29**, 2148 (1935). (197) Gibson, Harley-Mason, Litherland, Mann, *J. Chem. Soc.* **1942**, 172. (198) Eisleb (to I.G.), Ger. 473,219, March 13, 1929; *Cent.* **1929**, II 350; [*C.A.* **23**, 2987 (1929)]; Brit. 275,622, Sept. 28, 1927; *Cent.* **1929**, II 350; *C.A.* **22**, 2171 (1928). (199) Eisleb (to Winthrop Chem. Co.), U.S. 1,845,403, Feb. 16, 1932; *Cent.* **1932**, I 3112; *C.A.* **26**, 2199 (1932). (200) Ingold, Rothstein, *J. Chem. Soc.* **1931**, 1672–1673.

(201) M.L.B., Ger. 284,291, May 19, 1915; *Cent.* **1915**, I 110; [*C.A.* **10**, 94 (1916)]. (202) Reboul, *Compt. rend.* **93**, 423 (1881). (203) Schmidt, *Ann.* **337**, 116–121 (1904). (204) du Pont Co., Brit. 477,981, Feb. 10, 1938; *Cent.* **1938**, II 183; not in *C.A.* (205) Tronov, Gershevich, *J. Russ. Phys.-Chem* [illegible] *C.A.* **22**, 3389–3390 (1928). (206) Tronov, *J. R* [illegible] *ent.* **1927**, II 1145; *C.A.* **22**, 2737 (1928). (207) [illegible] 08) Fromm, *Ann.* **442**, 133–134, 142 (1925). (209) Ohle, Haeseler, *Ber.* **69**, 2325 (1936). (210) Gabriel, Ohle, *Ber.* **50**, 820–821 (1917).

(211) Tomita, *Z. physiol. Chem.* **158**, 42–57 (1926). (212) den Otter, *Rec. trav. chim.* **57**, 18–20 (1938). (213) Weizmann, Malkowa, *Bull. soc. chim.* (4) **47**, 357–358 (1930); *Compt. rend.* **190**, 495–496 (1930). (214) Lohmann, *J. prakt. Chem.* (2) **153**, 57–64 (1939). (215) Bachman, Mayhew, *J. Org. Chem.* **10**, 250, 253 (1945).

3:5360 1,2-DICHLOROBUTENE-2 (low-boilg. stereoisomer)



$C_4H_6Cl_2$ Beil. S.N. 11

B.P.	**116–118°** at 765 mm. (2)	D_4^{20} = **1.1544** (2)	n_D^{20} = **1.4642** (2)
	111.5–112.5° at 742 mm. (1)	D_4^{18} = **1.1550** (2)	n_C^{18} = **1.4576** (2)
		D_4^{16} = **1.1488** (1)	n_C^{16} = **1.45513** (1)

[*See also high-boilg. stereoisomer* (3:5615).]

[For prepn. of $\bar{C}$ (together with its stereoisomer (3:5615)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn. of $\bar{C}$ (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of Cl_2 at 350° see (3).]

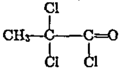
$\bar{C}$ with 1 mole Cl_2 + 1.5 moles $NaHCO_3$ at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

$\bar{C}$ on hydrolysis by htg. with 2 pts. aq. + 1 mole powdered $CaCO_3$ at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

$\bar{C}$ on oxidn. with $KMnO_4$ in acetone gives (1) chloroacetic acid (3:1370) + AcOH (1:1010) + HCl. — $\bar{C}$ in CCl_4 at −17° treated with O_3 followed by aq. gives acetaldehyde (1:0100).

3:5360 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 658–662 (1937); *Cent.* **1937**, II 371; *C.A.* **31**, 5754 (1937). (2) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1553–1558 (1936); *Cent.* **1937**, I 3786; *C.A.* **31**, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappij, Brit. 468,016, July 22, 1937; French 810,112, March 15, 1937; *Cent.* **1937**, II 4102. (4) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939). (5) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 663–666 (1937); *Cent.* **1937**, II 371; *C.A.* **31**, 5754 (1937).

3:5372 α,α-**DICHLOROPROPIONYL CHLORIDE** $C_3H_3OCl_3$ Beil. II - 251
II_1—
II_2-(228)



B.P. **117.4–117.8°** at 753 mm. (1) D_4^{20} = **1.4062** (1) n_D^{20} = **1.45240** (1)
110–115° (2)
68–73° at 88–90 mm. (3)

Colorless lachrymatory liq with penetrating odor.

[For prepn. of $\bar{C}$ from α,α-dichloropropionic acid (3:6162) with $SOCl_2$ under reflux for 10 hrs. (1) or with PCl_3 (2) see indic. refs., from pyruvic acid ($CH_3CO.COOH$) (1:1040) with PCl_5 see (2) (4).]

[For study of rate of reaction of $\bar{C}$ in dioxane with β-chloroethanol (3:5552) see (1).]

$\bar{C}$ with aq. readily hydrolyzes to α,α-dichloropropionic acid (3:6162) q.v.

Ⓓ α,α-**Dichloropropionamide:** lfts. from dil. alc., m.p. 117–118° (3) (5), 116–117° (2), 116° (4) [From $\bar{C}$ with conc. aq. NH_4OH (2); for other ways see under α,α-dichloropropionic acid (3:6162).]

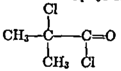
Ⓓ α,α-**Dichloropropion-*N*-ethylamide:** m.p. 51–52° (3). [From $\bar{C}$ with $EtNH_2$ (3).]

—— α,α-**Dichloropropionanilide:** m.p. 101° (3). [Reported only by indirect means (3).]

—— α,α-**Dichloropropion-*p*-toluidide:** m.p. 84–86° (6). [Reported only by indirect means (6).]

3:5372 (1) Leimu, *Ber.* **70**, 1046, 1050 (1937). (2) Beckurts, Otto, *Ber.* **11**, 386–391 (1878). (3) von Braun, Jostes, Münch, *Ann.* **453**, 126, 135 (1927). (4) Klimenko, *Ber.* **3**, 465–468 (1870). (5) Otto, *Ann.* **132**, 183 (1864). (6) Bischoff, Walden, *Ann.* **279**, 93 (1894).

3:5385 α-**CHLORO-ISOBUTYRYL CHLORIDE** $C_4H_6OCl_2$ Beil. II - 295
II_1—
II_2-(263)



B.P. **117–118°** (1) n_D^{20} = **1.4369** (1)
113–114° (2)

The b.p. of 125–126° given by (3) is incorrect (1).

[For prepn. of $\bar{C}$ from isobutyryl chloride (3:7270) with Cl_2 (3) (4) (5) or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (20% $\bar{C}$ + 80% β-chloro isomer (1)) see indic. refs.; for prepn. of $\bar{C}$ from α-hydroxyisobutyric acid (1:0431) with $SOCl_2$ (together with other products) see (2).]

[For reactn. of $\bar{C}$ with MeOH yielding methyl α-chloro-isobutyrate (3:7918) see (5).]

$\bar{C}$ on hydrolysis with aq. yields α-chloro-isobutyric acid (3:0235) q.v.

3:5385 (1) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (2) Blaise, Montagne, *Compt. rend.* **174**, 1555 (1922). (3) Michael, Garner, *Ber.* **34**, 4054–4055 (1901). (4) Henry, *Compt. rend.* **142**, 1024 (1906); *Bull. acad. roy. Belg.* **1906**, 206–226; *Cent.* **1906**, II 227. (5) du Pont Co. & Loder, Brit. 428,223, May 9, 1935; *Cent.* **1936**, I 179; *C.A.* **29**, 6607 (1935).

3:5395 1,1,2-TRICHLOROPROPENE-1

$CH_3—C(Cl)=CCl_2$ $C_3H_3Cl_3$ Beil. I - 200 / I_1— / I_2—

B.P. 118°	(1)	
116–117°	(2)	$D^{14}_{14} = 1.387$ (3)
115°	(3)	

[For prepn. of $\bar{C}$ from 1,1,1,2-tetrachloropropane (3:5785) in 93% yield by htg. with aq. or alc. alk. for 3 hrs. at 95° see (1); for prepn. of $\bar{C}$ from 1,1,2,2-tetrachloropropane (3:5825) with alc. KOH or alc. NH_4OH see (2) (3).]

[For use of $\bar{C}$ as dry cleaner and spot remover (4) or in degreasing of metals (5); for use in dewaxing of mineral oils see (6).]

$\bar{C}$ with Cl_2 yields (3) 1,1,1,2,3-pentachloropropane (3:4740), m.p. 179°.

...it. 469,051, July 19, 1937; *Cent.* **1938**, I 1218; *C.A.* **32**, 596 ...28, 2668 (1895). (3) Borsche, Fittig, *Ann.* **133**, 117–119 ... U.S. 2,116,437, May 3, 1938; *Cent.* **1938**, II 796; *C.A* **32**, ... Co.), U.S. 2,116,438, May 3, 1938; *Cent.* **1938**, II 947; *C.A.* **32**, 4936 (1938). (6) Standard Oil Development Co., French 790,852, Nov. 28, 1935; *Cent.* **1936**, I 2672; *C.A.* **30**, 3323 (1936).

3:5420 TRICHLOROACETYL CHLORIDE

$Cl_3C—C(Cl)=O$ C_2OCl_4 Beil. II - 210 / II_1-(94) / II_2-(200)

B.P. 118° cor.		(1) (8)	$D^{20}_4 = 1.6202$ (3); $n^{20}_D = 1.4701$ (5);
117–118°	at 760 mm.	(2)	1.6179 (5) 1.46949 (3)
117.9°	at 754 mm.	(3)	
116.3–118.5°		(4)	
116.4°	at 755 mm.	(5)	
116–117°	at 726 mm.	(6)	

[For prepn. of $\bar{C}$ from trichloroacetic acid (3:1150) with PCl_3 (1) (7) (8), with PCl_3 + $ZnCl_2$ (25% yield (9)), with $SOCl_2$ (yield: 12% (9), 30% (23)) in C_6H_6 (60% yield (3)) or in pyridine (90% yield (10)), with P_2O_5 + HCl gas (11), with benzotrichloride (3:6540) + $ZnCl_2$ at 100° (77% yield (12)), with benzoyl chloride (3:6240) (51–56% yield (13)) see indic. refs.]

[For formn. of $\bar{C}$ from trichloroacetic acid at 300° (together with CO, CO_2 + HCl) see (14); from acetyl chloride (3:7065) with 3 moles PCl_5 see (11); from hexachloroethane (3:4835) with SO_3 at 150° see (15); from pentachloroethane (3:5880) or *sym.*-tetrachloroethane (3:5750) in ultra-violet light and O_2 see (16); from tetrachloroethylene (3:5460) with SO_3 (15), with H_2SO_4 + HNO_3 (together with other products) (17), with ozone (18) (19), with oxygen in pres. of Br_2 or conc. HNO_3 (20), with oxygen by chlorine sensitized photo-oxidation (21) cf. (30) (31), or with oxygen in ultra-violet light (16) see indic. refs.; from diethyl ether on protracted chlorination in sunlight, from decachlorodiethyl ether (3:1676) on distn. see (22), or from distn. of pentachloroethyl trichloroacetate see (22), from CCl_4 (3:5100) + $AlCl_3$ + CO gas at 200° and 250 atm. (37% yield) see (32).]

[$\bar{C}$ on htg. (13) or on htg. with $AlCl_3$ (23) yields carbon tetrachloride (3:5100) + CO; $\bar{C}$ on htg. at 600° yields (24) carbon tetrachloride (3:5100) + hexachloroethane (3:4835) + CO + phosgene (3:5000).]

[$\bar{C}$ on treatment at −5° with dry HBr gas gives (70% yield (24)) trichloroacetyl bromide, b.p. 143°; $\bar{C}$ similarly treated with dry HI gas gives (71.5% yield (6)) trichloroacetyl iodide, b.p. 74–74.2° at 30 mm. (6).]

[C̄ with MeOH should yield readily methyl trichloroacetate (3:5800), b.p. 153.8°; C̄ with EtOH yields (1) ethyl trichloroacetate (3:5950), b.p. 168°. (For study of rate of reactn. see (2)).]

[C̄ with pure freshly distilled $AlCl_3$ + C_6H_6 yields (25) (26) triphenylvinyl alcohol (ω,ω-diphenylacetophenone) [Beil. VII-522, VII_1-(291)], m.p. 137°; with moist $AlCl_3$ + C_6H_6, however, C̄ gives instead (25) (27) (28) ω,ω,ω-trichloroacetophenone (3:6874), b.p. 256–257° (25). — C̄ with Me_2Zn yields (29) pentamethylethyl alcohol [Beil. I-418, I_1-(207), I_2-(447)]. — C̄ with EtMgBr in ether at 10° gives (33) 1,1,1-trichlorobutanol-2 (3:5955).]

C̄ hydrolyzes readily with aq. yielding trichloroacetic acid (3:1150); for the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see trichloroacetic acid (3:1150).

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(31) Kirkbride (to Imperial Chem. Ind., Ltd.), U S. 2,321,823, June 15, 1943; *C.A.* **37**, 6676 (1943): B [illegible] *C.A.* **37**, 4746 [illegible] 4085 (1945). [illegible]

3:5425 1-CHLOROPROPANONE-2 (Chloroacetone; acetonyl chloride) $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{Cl}{|}}{CH_2}$ C_3H_5OCl Beil. I - 653, I_1-(344), I_2-(718)

B.P.		B.P. (contd)		
119–120°	(1) (20)	60–62° at 60 mm.	(10)	D_4^{25} = 1.123 (189)
119.7° at 760 mm.	(2)	46° at 46 mm.	(3)	D_-^{20} = 1.170 (11)
119.5° (3)		35° at 29 mm.	(6)	D_{15}^{17} = 1.164 (12)
119.3°	(4)	20° at 12 mm.	(6)	
118.8–119.4°	(5)			D_{16}^{16} = 1.162 (7) cf. (189)
119° at 760 mm.	(6)			
119° at 736 mm.	(7)			D_{13}^{13} = 1.158 (9) cf. (189)
118° at 723 mm.	(8)			
117–118°	(9)			D_4^{15} = 1.135 (189)

C̄ when pure is colorless liq. — C̄ turns dark on exposure to light. — C̄ on long exposure to light, acids, or metals resinifies to a dark mass, m.p. above 350°, which fumes in air and dis. in fumg. HNO_3, but does not react with fumg. H_2SO_4, NH_2OH, or phenylhydrazine

nor hydrolyze with 50% KOH (13). — [For stabilization of C̄ by means of addn. of 1% $CaCO_3$ (14) or 0.1% aq. (15) see indic. refs.]

C̄ is sol. in 10 pts. aq. (7) but does *not* form crystn. hydrates with it (9) (for prepn. of anhydrous C̄ using $CaSO_4$ see (16)); C̄ is volatile with steam (9); sol. in alc., ether, $CHCl_3$. C̄ has very pronounced lachrymatory properties; for studies of this property see (17) (18).

C̄ forms azeotropes with several org. liqs. (19); e.g., C̄ with toluene (1:7405) forms a const.-boilg. mixt., b.p. 109.2° at 760 mm., contg. 28.5% C̄; C̄ with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 105.8° at 760 mm., contg. 36% C̄; C̄ with ethyl *n*-butyrate (1:3127) forms a const.-boilg. mixt., b.p. 117.2° at 760 mm., contg. 53% C̄; C̄ with isobutyl acetate (1:3115) forms a const.-boilg. mixt., b.p. 116.7°, contg. 30% C̄.

[For prepn. of C̄ from acetone (1:5400) with Cl_2 (188) (9) (20) (21) (22) (23) (24) (25) (yield is poor and contaminated with higher chlorination prods. especially 1,1-dichloropropanone-2 (*unsym.*-dichloroacetone) (3:5430) whose b.p. is very close to that of C̄); with Cl_2 in pres. of $CaCO_3$ (yield 82% (3)) (26) (27) (28); with Cl_2 in vapor-phase chlorination (29) (30) (21) in pres. of $NiCl_2$ (38); by electrolysis in HCl (97% yield (32)) (36) using Pt electrodes (with graphite or lead electrodes resultant C̄ is reduced) even using alternating current (35% yield (33)); with Cl_2O (34); with HOCl (22) (27) (35); with EtOCl (3:7022) (1); with *N*-chlorourea in aq. soln. (37); or with SO_2Cl_2 (72% yield (189)) see indic. refs.]

[For prepn. of C̄ from acetone (1:5400) with benzenediazonium chloride (solid) in pres. of $CaCO_3$ (39) (40), or with aq. solns. of other diazonium chlorides (especially those with negative substituents such as those from *p*-nitroaniline, *p*-chloroaniline, or 2,4-dichloroaniline) in pres. of $CuCl_2$ + NaOAc (41), see indic. refs.]

[For prepn. of C̄ from 1-chloropropanol-2 (propylene α-chlorohydrin) (3:7747) by oxidn with $K_2Cr_2O_7 + H_2SO_4$ (42) (43) (44) (45), CrO_3 + dil. H_2SO_4 (43), CrO_3/AcOH (43), HNO_3 (43) (44) (45), HOCl (42), or $Ca(OCl)_2$ (46) see indic. refs.; from 3-chloro-2-methylpropene-1 (methallylchloride) (3:7145) (10), or from 1-chloro-2-methylbutene-2 (3:7485) (47), or from 1,3-dichloro-2-methylpropene-1 (3:5590) (48), or from 1,4-dichloro-2-methylbutene-2 (3:9204) (49) with O_3 see indic. refs.]

[For prepn. of C̄ from ethyl γ-chloroacetoacetate (3:6375) (50) or from α-chloroacetoacetanilide (51) by hydrolytic cleavage with HCl see indic. refs.; from 1,3-dichloropropene-2 (3:5280) by soln. in conc. H_2SO_4 and distn. with aq. see (52); from allyl chloride (3:7035) with HgO + HOCl see (53); from 1,2-epoxypropane (propylene oxide) (1:6115) with Cl_2 at 0° see (54); from diketene + Cl_2 in cold followed by treatment with aq. see (55).]

[For use of C̄ in refining of mineral oils see (56); in prepn. of photosensitizing cyanine dyes see (57).]

Pyrolysis. [C̄ passed through tube at 450° pyrolyzes into acetaldehyde (1:0100), acetone (1:5400), crotonaldehyde (1:0150) + HCl (58).]

Reduction. [C̄ on reduction with Zn + HCl (7) or on electrolysis in HCl soln. using graphite or lead electrodes (32) yields acetone (1:5400); C̄ on reduction with $AlEt_3$ etherate as directed (59) gives (70% yield) 1-chloropropanol-2 (3:7747), b.p. 78–81° at 80 mm. (59); C̄ on phytochemical reduction using yeast (60) gives (25% yield) 1-chloropropanol-2 (3:7747); for polarographic study of oxidn.-reductn. potential of C̄ see (61).]

Oxidation. C̄ on oxidn. with $KMnO_4$ (49) (62), HNO_3, CrO_3, etc. (62), yields chloroacetic acid (3:1370) and AcOH (1:1010). — C̄ with moist silver oxide yields (7) glycolic acid (1:0430), acetic acid (1:1010), and formic acid (1:1005).

Halogenation. [C̄ with Cl_2 even in cold gives (26) more highly chlorinated acetones; e.g., C̄ with Cl_2 at 30–40° yields (63) 1,1,3-trichloropropanone-2 (3:5957) and 1,1,1-trichloropropanone-2 (3:5620); C̄ with Cl_2 at 50–70° yields (63) cf. (64) *sym.*-tetrachloro-

acetone (3:6050), *unsym.*-tetrachloroacetone (3:6085), and pentachloroacetone (3:6205); C̄ with Cl_2 at 50–100° in light (63) (65) or under press. (66) yields hexachloroacetone (3:6312). — Note that C̄ with $Ca(OCl)_2$ undergoes both chlorination and subsequent cleavage yielding (46) $CHCl_3$ (3:5050).]

[C̄ with Br_2 (3 moles) at 100° yields (67) 3,3,3-tribromo-1-chloropropanone-2 [Beil. I-658], b.p. 215°, 13.0° at 25 mm.]

Reactions of the halogen atom of C̄ (see also further below under formn. of heterocyclic systems). C̄ with excess aq. alkali presumably yields propanone-2-ol-1 (acetol) (1:5455) and therefore reduces Fehling's soln.; the halogen atom of C̄ is so reactive that C̄ slowly neutralizes 1 equiv. alk. (68); C̄ with NaOEt in abs. alc. yields acetol ethyl ether (ethoxyacetone) [Beil. I-822, I_1-(418), I_2-(867)], b.p. 128° at 760 mm. (for study of rate of reaction see (69)).

[C̄ with phenol (1:1420) + anhydrous K_2CO_3 in acetone stirred 24 hrs. at room temp. *or refluxed 3 hrs.* (70) (*note that in pres of KI yield jumps to 92.5%* (191)), *or* C̄ *with* sodium phenolate in phenol (71) (72) or in toluene (73), gives (yields: 21–23% (70), 16% (73)) phenoxyacetone (1:5534), b.p. 117–124° at 19 mm. (70) (note that C̄ + phenol + aq. NaOH gives only black resin (73)) (for application of this type of reactn. to other monohydric phenols such as tetralol-2 (5,6,7,8-tetrahydronaphthol-2) (74) (75) or *p-ter*-butyl)phenol (1:1510) (75) or β-naphthol (1:1540) (191) see indic. refs.). — Note that C̄ with phenol (3 moles) + fumg. HCl at 100° reacts in a dif. sense to give (50% yield (76)) a *tris*-(hydroxyphenyl)propane of undetd. struct.; for formn. of resins from C̄ + phenol see (77) (78).]

[C̄ with KI in aq. MeOH (79) (80) or in acetone (5) gives (75% yield (80)) iodoacetone [Beil. I-660, I_1-(345), I_2-(719)], oil, b.p. 58.4° at 11 mm. (79) (oxime, pr. from pet. eth., *m.p.* 64.5° (79)); *for study of rate of this reactn. in acetone at* 0° *and* 10° *see* (5). — C̄ with K_2SO_3 (or Na_2SO_3) yields (81) salts of acetonesulfonic acid [Beil. IV-19, IV_2-(530)]. — For study of rate of reactn. of C̄ with aq. $Na_2S_2O_3$ see (82). — C̄ with Na_2S in acetone yields (83) (84) *bis*-(acetonyl) sulfide, m.p. 49° (83), b.p. 126° at 14 mm. (83), 125° at 18 mm. (84) (earlier work (85) using alc. as solvent could not be checked (83) (84).)]

[C̄ with aq. NaSCN stirred 10 hrs. at 25° (86), or C̄ with $Ba(SCN)_2$ directly (87) or in alc. (88) (89) cf. (90), gives (95% yield (86)) thiocyanoacetone (acetonyl thiocyanate) [Beil. III-179, III_1-(72), III_2-(125)], oil, b.p. 73.5–74.5° at 1 mm. (86), $D_{15}^{15} = 1.1892$ (86) (for use of this prod. as anti-oxidant for rubber (91), as stabilizer for cellulose (92), or as 1% soln. in petroleum as insecticide (93) see indic. refs.); note that thiocyanacetone, although insensitive to dil. aq. HCl (87), with HCl gas in cold (86) or conc. HCl on boilg (89) adds 1 mole HCl and ring-closes to 2-chloro-4-methylthiazole, oil, b.p. 167–167.5° at 754 4 mm., 69° at 14 mm. (86); note also that thiocyanoacetone with aq. $NaHCO_3$ (94) (or C̄ + aq. KSCN + $NaHCO_3$ (86)) yields 2-hydroxy-4-methylthiazole (4-methylthiazolone-2) ("α-methylrhodime") [Beil. XXVII-158, $XXVII_1$-(264)], ndls. from aq. or ether, m p. 105–106° (94), 102–103° (86).]

[C̄ with Na salts of sulfinic acids gives the corresp. alkyl- (or aryl)sulfonylacetones: e.g., C̄ with Na methanesulfinate gives (95) methanesulfonylacetone, m.p. 64° (95) (96); C̄ with Na benzensulfinate in alc. gives on refluxing (95% yield (97)) benzenesulfonylacetone [Beil. VI-307, VI_1-(145)], lfts. from alc., m p. 57° (97); C̄ with Na *p*-toluenesulfinate yields (97) *p*-toluenesulfonylacetone [Beil. VI-421, VI_1-(210)], m p. 51° (97) (98); many other analogous cases are known.]

[C̄ with tertiary amines gives the corresp. quaternary ammonium chloride salts: e.g., C̄ with dry Me_3N in abs. ether (99) or abs. alc. (100) (101) yields trimethyl-acetonylammonium chloride [Beil. IV-315, IV_2-(763)], very hygroscopic white solid; C̄ with pyridine gives corresp. salt (for study of rate in abs. alc. at 55.6° see (102)). — C̄ with triphenyl-

phosphine in C_6H_6 at 75–80° for 15 hrs. yields (103) triphenyl-acetonyl-phosphonium chloride, m.p. 234° dec. (103). — $\bar{C}$ with hexamethylenetetramine in $CHCl_3$ grad. ppts. an addn. prod. (poor yield (104)), ndls., m.p. 122° (104).]

[$\bar{C}$ with dry NH_3 may yield (9) a little aminoacetone (acetonylamine) [Beil. IV-314, IV_1-(450), IV_2-(763)], but the reactn. is unsatisfactory and other methods (105) are preferred for prepn. of the latter; $\bar{C}$ (in excess) with aq. soln. (30%) of Me_2NH yields (106) dimethylaminoacetone [Beil. IV-314], misc. with aq., alc., ether, b.p. 123° (106); $\bar{C}$ (1 mole) with Et_2NH (2 moles) in ether yields (106) diethylaminoacetone [Beil. IV-316], b.p. 155–156° (106). — Many analogous cases are recorded.]

Reactions of $\bar{C}$ involving the H atoms of its $-CH_2Cl$ grouping. $\bar{C}$ with salicylaldehyde (1:0205) in alc. KOH refluxed for 15 min. (107) (108), or in alc. NaOH refluxed 2 hrs. (109), or $\bar{C}$ + Na salt of salicylaldehyde in dry C_6H_6 under reflux (110), gives (yields: 60–85% (107), 75% (109), 60% (108)) 2-(acetyl)coumarone (2-acetobenzofuran) [Beil. XVII-338], colorless lfts. from alc., m.p. 76° (107), 75–76° (109), 74–75° (108) (110) (corresp. oxime, ndls. from dil. alc., m.p. 150° (111), phenylhydrazone, cryst. from alc., m.p. 153–154° (107), semicarbazone, ndls. from dil. alc., m.p. 217° (107)). — $\bar{C}$ with *p*-dimethylaminobenzaldehyde in AcOH with HCl gas yields (112) α-chloro-α-(*p*-dimethylaminobenzal)acetone, yel. lfts. from alc., m.p. 115° (112) (corresp. phenylhydrazone, m.p. 206–208° (112), semicarbazone, m.p. 202–203° (112)), accompanied by a little α-chloro-α,α'-*bis*-(*p*-dimethylaminobenzal)acetone, cryst. from 1:1 abs. alc. + C_6H_6, m.p. 225° (112). — $\bar{C}$ with diazotized aniline in pres. of NaOAc at 0° yields (113) (49) cf. (114) 1-(benzeneazo)-1-chloroacetone [Beil. XV-342], yel. ndls. from boilg. alc., m.p. 136–137° (113), 135–136° (49).

Reactions of $\bar{C}$ involving the keto group. $\bar{C}$ with satd. aq. $NaHSO_3$ soln. yields (51) a crystn. $NaHSO_3$ cpd. cf. (7).

[$\bar{C}$ with HCN as directed gives (yields: 94% (119), 87–90% (192)) (21) (115) (116) β-chloro-α-hydroxyisobutyronitrile (chloroacetone cyanohydrin) [Beil. III-317], oil, b.p. 110° at 22 mm. (117) 108–110° at 20 mm. (192), 103–104° at 16 mm. (115), $D^{15}_{-} = 1.2027$ (117), $n^{20}_D = 1.4520$ (192), $n^{11}_D = 1.45362$ (117); this prod. on distillation at ord. press. or even on stdg. in the air readily dissociates into the original components; on saponification with HCl, however, it gives (62% yield (192)) (5) (115) β-chloro-α-hydroxyisobutyric acid [Beil. III-317, III_1-(120), III_2-(224)], ndls. from C_6H_6, m.p. 110° (118) 109–110° (192). — $\bar{C}$ (1 mole) with aq. KCN (1 mole) gives 43% yield (119) of a cpd., $C_8H_{10}O_2N_2$, m.p. 183°, formerly supposed to be α-aceto-β-hydroxy-β-methylglutaro(di)nitrile [Beil. III-883] but now (119) regarded as 2,4-dicyano-2,5-dimethyl-5-hydroxytetrahydrofuran (for mechanism of its formn. and review of earlier literature see (119)).]

[$\bar{C}$ forms acetals or similar cpds.: e.g., $\bar{C}$ with triethyl orthoformate (1:3241) in EtOH + a drop of H_2SO_4 gives (yields: 90% (120), 87% (80)) cf. (190) chloroacetone diethylacetal [Beil. I-654, I_2-(718)], b.p. 161–162° u.c. (120) 81–82° at 50 mm. (190), 52–53° at 14 mm. (80), $D^{14}_0 = 1.002$ (120); for acetals from $\bar{C}$ with glycerol (1:6540) (121) or pyrocatechol (1:1520) (122) see indic. refs.]

[$\bar{C}$ with phenyl isocyanide + AcOH in ether gives (123) α-acetoxy-β-chloroisobutyranilide; $\bar{C}$ with phenyl isocyanide + BzOH in ether gives (123) α-benzoyloxy-β-chloro-isobutyranilide.]

[$\bar{C}$ with RMgX cpds. (1 mole) in ether in general reacts normally with the ketonic group to give addn. prods. which with aq. yields the corresp. tertiary alcs.: e.g., $\bar{C}$ with MeMgBr gives (38% yield (124)) (125) 1-chloro-2-methylpropanol-2 (α-isobutylene chlorohydrin) (3:7752) (accompanied as a result of reactn. of a second MeMgBr and rearr. (126) (127) by some 2-methylbutanol-2 (1:6160)); for corresp. reactn. of $\bar{C}$ with EtMgBr yielding

1-chloro-2-methylbutanol-2 (3:8175) see (128); for corresp. reactn. of C̄ with n-C_3H_7MgBr, n-C_4H_9MgBr, iso-C_4H_9MgBr, iso-$C_5H_{11}MgBr$, n-$C_6H_{13}MgBr$, and n-$C_7H_{15}MgBr$ see (129); for corresp. reactn. of C̄ with *ter*-butylethynyl MgBr (130), with n-amylethynyl MgBr (131), or with ethynyl *bis*-(MgBr) (132) see indic. refs. — C̄ with C_6H_5MgBr yields (133) 1-chloro-2-phenylpropanol-2 [Beil. VI-507]; note, however, that if the initial addn. cpd. is htd. at 130–140° prior to hydrolysis rearr. occurs and the prod. then (134) is phenylacetone (1:5118). — For reactn. of C̄ with o-xenyl MgI see (70).]

[C̄ with abs. diazomethane (free from MeOH) in dry ether yields (135) 1-chloro-2-methyl-2,3-epoxybutane, b.p. 124° (135).]

Condensation reactions of C (usually yielding heterocyclic compounds). [C̄ with acetaldehyde (1:0100) + NH_4OH in pres. of $Cu(OAc)_2$ gives (49% yield (136)) 2,4-(or 5)-dimethylimidazole [Beil. XXIII-79, $XXIII_1$-(25)], b.p. 266° at 733 mm., m.p. 92° (136) (B̄.HCl, m.p. 205, B̄.PkOH, m.p. 142–143° (136)).]

[C̄ with methyl acetoacetate (1:1705) + NH_4OH at −1° gives (16% yield (137)) 3-carbomethoxy-2,5-dimethylpyrrole [Beil. XXII-29], cryst. from alc., m.p. 119.5°; C̄ with ethyl acetoacetate (1:1710) + excess conc. aq. NH_4OH (138) (140) or in ether with NH_3 gas (139) gives (yields: 44% (139), 20% (138)) 3-carbethoxy-2,5-dimethylpyrrole [Beil XXII-29, $XXII_1$-(496)], m.p. 116–117° (138) (other by-prods. also being formed (139)); C̄ with ethyl acetoacetate (1:1710) + prim. amines similarly gives N-substituted analogs; e.g., use of aq. $MeNH_2$ gives (141) 3-carbethoxy-1,2,5-trimethylpyrrole [Beil. XXII-29, $XXII_1$-(496)], m.p. 48° (141); use of aniline gives (139) (141) 3-carbethoxy-2,5-dimethyl-1-phenylpyrrole [Beil. XXII-30, $XXII_1$-(496)], m.p. 43°, b.p. 225° at 40 mm.; for corresp. use of p-toluidine see (141).]

[C̄ with ethyl oxaloacetate [Beil. III-780, III_1-(273), III_2-(479)] in ether treated with NH_3 *gas yields (139) 4-carbethoxy-5,6-dihydroxy-2(or 3)-methylpyridine* [Beil. XXII-259], m.p. 223° (139) (much oxamide and other by-prods. also being formed).]

[C̄ with diethyl acetonedicarboxylate (1:1772) in ether (142) (143) (139) or C_6H_6 (144) with dry NH_3 gas gives (yields: 49% (143), 38% (142)) ethyl (3-carbethoxy-4-methylfuryl-2)acetate [Beil. XVIII-333], oil, b.p. 168° at 20 mm. (139).]

[C̄ htd. with amides yields corresp. oxazoles: e.g., C̄ with acetamide htd. 8–10 hrs. at 120° under reflux gives (7% yield (145)) (146) 2,4-dimethyloxazole [Beil. XXVII-17], liq. with odor like pyridine, very sol. aq., b.p. 108° (145) (146); C̄ with benzamide + powdered $CaCO_3$ at 115–120° for 8 hrs. gives (15% yield (147)) (148) 2-phenyl-4-methyloxazole [Beil. XXVII-58], b.p. 238–241° (148), 92–95° at 5 mm. (147) (B̄.HCl, m.p. 72°, B̄.PkOH, m.p. 111° (147)); for corresp. reactn. of C̄ with m-nitrobenzamide see (147).]

[C̄ with thioamides yields corresp. thiazoles: e.g., C̄ with thioformamide in abs. alc. refluxed for 1 hr. (149) or C̄ with formamide + P_2S_5 (150) gives (35–47% yield (149)) 4-methylthiazole [Beil. XXVII-16], b.p. 131° (150), 130° (149), 70–71° at 59 mm. (151) (B̄.PkOH, m.p. 181° (151); B̄.EtI, m.p. 144.5° (149)); C̄ with thioacetamide without solvent (152) (153) in aq. or alc. (152) (149) or C̄ with acetamide + P_2S_5 (150) yields 2,4-dimethylthiazole [Beil. XXVII-18], b.p. 144–145.5° cor. at 719 mm. (152), 143–144° at 762 mm. (153), 143° (150) (154), D_4^{20} = 1.0562 (B̄.PkOH, m.p. 137–138° (152), B̄.EtI, m.p. 212° dec. (149)); C̄ with thiobenzamide in alc. gives (155) (147) 4-methyl-2-phenylthiazole [Beil. XXVII-58], m.p. 29.5° (156), b.p. 282° at 762 mm. (156), 275–277° at 750 mm. (147), 111° at 6 mm. (147); many other analogous cases are recorded.]

[C̄ with aq. thiourea (157) (158) (159) or C̄ with NH_4SCN (160) (161) or C̄ with NH_4SCN + NH_4OH (162) (86) gives (70–75% yield (157)) 2-amino-4-methylthiazole [Beil. XXVII-159], m.p. 44–45° (157), 42° (159), b.p. 231–232° sl. dec. (162), 130–133° at 18 mm. (157), 117–120° at 8 mm. (157); C̄ with N-methylthiourea gives (163) (164) (158) 2-(methyl-

amino)-4-methyl-thiazole [Beil. XXVII-159], pr. from alc., m.p. 71.5–72.5° cor. (163), 64° (164) (B̄.HCl, m.p. 228° cor. (163)); C̄ with phenylthiourea gives (158) (164) 2-(anilino)-4-methylthiazole [Beil. XXVII-159], ndls. from alc., m.p. 117–118° (164), 115° (158).]

[C̄ with *O*-methyl thiocarbamate on warming gives (89) 2-methoxy-4-methylthiazole, b.p. 59–60° at 18 mm. (89) (B̄.HCl, m.p. 78°; B̄.$HgCl_2$, m.p. 123–124° (89)) (accompanied by its dimer); C̄ with *O*-ethyl thiocarbamate + KOAc yields (89) 2-ethoxy-4-ethylthiazole, b.p. 71–72° at 15 mm. (89).]

[C̄ with solid ammonium dithiocarbamate in abs. alc. stood at room temp. for 12 hrs. then refluxed 1 hr. gives (85% yield (151)) 2-mercapto-4-methylthiazole [Beil. XXVII-161], cryst. from isopropyl ether/alc. or dil. alc., m.p. 89–90° (165), 88.0–88.5° (151); note that in ether these reactants yield (166) an intermediate *S*-acetonyl dithiocarbamate, m.p. 80–82° (166), which on stdg. changes to the above 2-mercapto-4-methyl-thiazole; for use of the latter (or its metal salts) as vulcanization accelerators see (167).]

[C̄ with 1-phenylthiosemicarbazide in abs. alc. readily dis. at room temp. yielding on addn. of pyridine (168) 2-(phenylhydrazino)-4-methylthiazole, m.p. 170° (acetyl deriv., m.p. 170° (168)); for analogous reactions of C̄ with the three 1-(tolyl)thiosemicarbazides (169), the three 1-(nitrophenyl)thiosemicarbazides (170), see indic. refs.]

[C̄ with acetone thiosemicarbazone in $CHCl_3$ gives on warming (171) the corresp. deriv. of 4 methylthiazolone 2, viz., 2-keto-4-methyl-2,3-dihydrothiazole-2-isopropylidenehydrazone; for analogous reactn. of C̄ with acetophenone thiosemicarbazone and benzaldehyde thiosemicarbazone see (171).]

Ⓟ **Color reactn. with KOH:** C̄ with excess very conc. aq. KOH gives crimson red color (5) (22).

—— **Acetonyl acetate** (acetol acetate) (acetoxyacetone) [Beil. II-155, II_1-(72), II_2-(168)]: b.p. 174–175° at 760 mm. (172), 137–138° at 230 mm. (172), D_4^{20} = 1.0749, n_D^{20} = 1.4150 (Beil.). [From C̄ + KOAc in MeOH (173) or abs. EtOH (172) after 2 hrs. reflux (82% yield (173)).]

—— **Acetonyl benzoate** (acetol benzoate) (benzoyloxyacetone) [Beil. IX-148]: m.p. 23.5–24° (174), 25° (175); b.p. 188–190° at 60 mm. (176). [From C̄ with KOBz on htg. together (54% yield (176)) or in alc. soln. (174).]

Ⓓ **1-(β-Naphthoxy)acetone** (acetonyl β-naphthyl ether): cryst. from alc., m.p. 78.4° cor. (177), 78° (178), 69–73° (191), 69–72° (70). [From C̄ + Na β-naphtholate on htg. in β-naphthol (178) or from C̄ + β-naphthol (1:1540) + dry K_2CO_3 refluxed in acetone (21% yield (70)) (note that by addn. of KI yield jumps to 85% (191)).]

Ⓓ **1-(*N*-phthalimido)acetone** (*N*-acetonylphthalimide) [Beil. XXI-477, XXI_1-(371)]: lfts or ndls. from aq., m.p. 124° (105). [From C̄ + K phthalimide at 120° for 20 min. (179) or refluxed 1 hr. in xylene (67% yield (180)).]

Ⓓ **1-(*N*-3-nitrophthalimido)acetone** (*N*-(acetonyl)-3-nitrophthalimide: ndls. from alc., m.p. 152–153° (181). [From C̄ with K 3-nitrophthalimide on htg. (181).]

Ⓓ **Methylglyoxal dioxime** (methylglyoxime) [Beil. I-764, I_1-(396), I_2-(822)]: pr. from alc., m.p. 156° (182). [From C̄ with aq. soln. contg. $NH_2OH.HCl$ (3 moles) + Na_2CO_3 (2 moles) followed by acidification and ether extraction (182); note that by careful regulation of conditions chloroacetone oxime has been obtd. (82% yield (183)), but since it is an oil, b.p. 171° at 727 mm. with slight decompn., it has no value as a Ⓓ for C̄.]

Ⓓ **1-(β-Phenylhydrazino)acetone phenylhydrazone** [Beil. XV-412]: yel. cryst. from MeOH, m.p. 162.5° (184). [From C̄ with phenylhydrazine (3 moles) in abs. alc. at −10 to −18° (184).]

Ⓓ **Chloroacetone *o*-nitrophenylhydrazone:** m.p. 83° (135).

Ⓓ **Chloroacetone 2,4-dinitrophenylhydrazone:** yel. ndls. from alc., m.p. 124.0–125.5° (185) (51), 124° (39). [From $\bar{C}$ (0.5 g.) with 2,4-dinitrophenylhydrazine (1.0 g.) in alc. (12 ml.) + conc. HCl (1.5 g.) under reflux (185); note that this prod. on protracted (13 hrs.) boilg. in alc. disproportionates yielding (185) $\bar{C}$ + 2,4-dinitrophenylhydrazine (both sol. hot alc) accompanied by the spar. sol. methylglyoxal-*bis*-(2,4-dinitrophenyl)-osazone, cryst. from pyridine, m.p. 298° (185), for various other reactans. see (185).]

Ⓓ **Chloroacetone semicarbazone:** m.p. 147–148° dec. (39), 141–142° (47), 136–137° (48), 165° (50), 163–165° (44). [From $\bar{C}$ with aq. semicarbazide HCl on addn. of solid $NaHCO_3$ at room temp. (186); note that this prod. is reactive and on boilg. with aq. dissolves to a bright yel. soln. which soon becomes colorless and ppts. hydrazine dicarboxylic acid diamide leaving in the filtrate hydroxypropanone semicarbazone, m.p. abt. 192° dec. (186); these changes (which doubtless occur slowly even on standing in water at room temp.) probably account for the divergent values of m.p. reported above.]

Ⓓ **Condensation prod.** ($C_{17}H_{20}O_4N_3SCl$) of $\bar{C}$ with *N*-methyl-β-carbohydrazidopyridinium *p*-toluenesulfonate: cryst. from 1.1 alc./ether, m.p. 135° cor. (187). [From $\bar{C}$ + indicated react. in abs. alc. on refluxing 15 min. (187).]

3:5425 (1) Goldschmidt, Endres, Dirsch, *Ber.* **58**, 576 (1925). (2) Lecat, *Rec. trav. chim.* **46**, 245 (1927). (3) Justoni, *Chimica e industria* (Italy) **24**, 89–94 (1942), *Cent* **1943**, I 383. (4) Cheng, *Z. physik. Chem.* **B-26**, 296 (1934). (5) Conant, Kirner, Hussey, *J. Am. Chem Soc.* **47**, 497 (1925). (6) Herbst, *Kolloidchem Beihefte* **23**, 330–331 (1927). (7) Linnemann, *Ann.* **134**, 170–175 (1865). (8) Mohler, *Helv. Chim Acta* **21**, 69 (1938). (9) Cloëz, *Ann. chim.* (6) **9**, 156–161 (1886). (10) Jacob, *Bull. soc. chim* (5) **7**, 581–586 (1940); *C.A.* **36**, 3508 (1942).

(11) Harkins, Clark, Roberts, *J. Am. Chem. Soc.* **42**, 703 (1920). (12) Dobrosserdow, *J. Russ. Phys.-Chem. Soc.* **43**, 129 (1911), *Cent.* **1911**, I 955. (13) Giua, Racciu, *Atti accad. sci.* [illegible] (1933). [illegible] (15) [illegible] 1941). (16) Wallis, Falck (to I G.), Ger 584,776, Oct 1, 1934, *Cent.* **1935**, I 156. (17) Bertrand, *Compt rend.* **171**, 965–967 (1920); *Cent.* **1921**, I 779. (18) Dufraisse, Bongrand, *Compt. rend.* **172**, 817–819 (1920), *Cent.* **1921**, I 1006. (19) Lecat, *Ann. soc. sci Bruxelles*, **47**, 21–27 (1927); *Cent* **1927**, II 226. (20) Glutz, Fischer, *J. prakt. Chem.* (2) **4**, 52–53 (1871).

(21) Bischoff, *Ber.* **5**, 863–867, 963–964 (1872). (22) Mulder, *Ber.* **5**, 1009–1010 (1872). (23) Bischoff, *Ber.* **8**, 1330 (1875). (24) Barbaglia, *Ber* **7**, 467 469 (1874). (25) Tcherniac, *Ber.* **25**, 2629–2632 (1892). (26) Fritsch, *Ber.* **26**, 597–598 (1893); *Ann.* **279**, 310–319 (1894). (27) Kling, *Bull. soc. chim.* (3) **33**, 322–324 (1905), *Ann. chim.* (8) **5**, 474–480 (1905). (28) Ger. 69,039, April 19, 1893; *Friedländer* **3**, 9 (29) Justoni, *Chimica e industria* (Italy) **24**, 195–201 (1942); *Cent.* **1943**, I 1659. (30) I.G., French 813,131, May 26, 1937; *Cent.* **1937**, II 2071.

(31) Rahrs (to Eastman Kodak Co.), U S. 2,235,562, March 18, 1941, *C.A.* **35**, 4040 (1941). (32) Szper, *Bull. soc. chim.* (4) **51**, 653–654 (1932). [illegible] 147–158 (1939); *Cent.* **1939**, II 3056; *C A.* **33**, 6727 [illegible] **58**, 567 (1925). (35) Richard, *Compt. rend.* **133**, 8[illegible] (1859). (37) Behal, Detoeuf, *Compt. rend.* **153**, 12[illegible] *Chem. Research (Tokyo)* **12**, 329–340 (1933); *Cent.* [illegible] Waters, *J. Chem. Soc.* **1937**, 2011–2012. (40) Water[illegible]

(41) Meerwein, Büchner, van Emster, *J. prakt. Chem.* (2) **152**, 248–251 (1939). (42) Markownikoff, *Ann.* **153**, 254–255 (1870). (43) Morley, Green, *J. Chem. Soc.* **47**, 133 (1885); *Ber.* **18**, 24–25 (1885). (44) Michael, *J. prakt. Chem.* (2) **60**, 455–457 (1899); *Ber.* **39**, 2787 (1906). (45) Henry, *Rec trav. chim.* **22**, 337–338 (1903); *Bull. acad. roy. Belg.* **1903**, 397–431; *Cent.* **1903**, [illegible] 47) Gutner, Tishchenko, [illegible] (48) Tishchenko, *J. Gen.* [illegible] Williams, *J. Chem. Soc.* [illegible]

(other prods. are also formed) or by electrolysis in HCl (9) see indic. refs.; from ethyl α,α-dichloroacetoacetate [Beil. III-663, III_1-(233), III_2-(427)] by ketonic cleavage with dil. HCl in s.t. at 170–180° for 4–6 hrs. (14) or by refluxing 4–5 hrs. with HCl (15) cf. (4) see indic. refs.; for formn. of C̄ from isopropyl alc. (1:6135) with Cl_2 see (16); from methylacetylene with HOCl (42% yield) see (17); from 1,1-dichloro-2-methylpropene-2 (3:7480) with O_3 see (18); from homoaspartic acid [Beil. IV-494, IV_1-(541), IV_2-(912)] by oxidn. with sodium *N*-chloro-*p*-toluenesulfonamide see (19).

[C̄ on reduction with $Al(OEt)_3$ + anhydrous acetaldehyde in dry ether gives (45% yield (20)) 1,1-dichloropropanol-2 (3:5755), b.p. 146–148°. — C̄ on reduction by yeast gives (54% yield (21)) levorotatory 1,1-dichloropropanol-2.]

C̄ on oxidn. with conc. HNO_3, CrO_3, or $KMnO_4$ yields (22) dichloroacetic acid (3:6208).

[C̄ with Br_2 (1 mole) (1) yields 3-bromo-1,1-dichloropropanone-2 [Beil. I-657], b.p. 111° at 25 mm. (1); C̄ with excess Br_2 at 100° yields (1) 3,3-dibromo-1,1-dichloropropanone-2 [Beil. I-658], b.p. 120° at 25 mm. (1); for study of rate of bromination of C̄ and influence of catalysts thereon see (4).]

[C̄ with PCl_5 htd. at b.p. of mixt. for 2 days yields (2) 1,1,2,2-tetrachloropropane (3:5825), b.p. 153°.]

[C̄ with aq. in s.t. at 200° for 6 hrs. yields (23) lactic acid (1:0400). — C̄ with aq. alk. yields (presumably via cleavage of the expected methylglyoxal) acetic acid (1:1010) and formic acid (1:1005); by virtue of this result C̄ readily reduces Fehling's soln. (24). — C̄ with aq. 10% K_2CO_3 on boilg. loses HCl yielding (25) acrylic acid (1:1020).]

C̄ with satd. aq. $NaHSO_3$ soln. readily yields (1) (5) an addn. prod. crystg. as a trihydrate.

[C̄ with conc. aq. HCN slowly dis. on protracted refluxing yielding (10) the corresp. cyanohydrin (β,β-dichloro-α-hydroxy-isobutyronitrile) [Beil. III-318], an oil, which on htg. dissociates into its components; this prod., however, on hydrolysis with strong HCl yields (10) the corresp. acid, β,β-dichloro-α-hydroxyisobutyric acid (3:2145), pr. from alc./ether or cryst. from C_6H_6, m.p. 82–83° (10) (26). — Note also that C̄ with phenylisocyanide + aq. on stdg. yields (26) β,β-dichloro-α-hydroxy-isobutyranilide, pr. from $CHCl_3$, m.p. 132–133° (26).]

[C̄ in excess MeOH (5 moles) with ethyl iminoformate hydrochloride (1¼ moles) 4–8 days at room temp. yields (27) *unsym.*-dichloroacetone dimethylacetal, b.p. 170–171° at 767 mm., 63° at 9 mm. — C̄ in excess EtOH with ethyl iminoformate as above yields (27) *unsym.*-dichloroacetone diethylacetal, b.p. 183–184° at 767 mm., 76° at 8 mm.]

[C̄ with *o*-nitrobenzaldehyde in alc. treated dropwise with aq. 5% NaOH condenses yielding (28) ω,ω-dichloro-*o*-nitrobenzalacetone, pptd. as oil by addn. of aq., colorless pr. from C_6H_6, m.p. 106–107° (28). — By similar procedure C̄ with *m*-nitrobenzaldehyde gives (28) ω,ω-dichloro-*m*-nitrobenzalacetone, colorless pr. from C_6H_6, m.p. 116–117°; C̄ with *p*-nitrobenzaldehyde similarly gives (30% yield (28)) ω,ω-dichloro-*p*-nitrobenzalacetone, colorless pr. from C_6H_6 or ether, m.p. 125°.]

[C̄ with diazotized aniline in pres. of NaOAc yields (29) dichloro-*bis*-(benzeneazo)-methane, yel.-or. cryst. from hot alc., m.p. 81–82°; C̄ with diazotized *p*-toluidine in pres. of NaOAc yields (29) dichloro-*bis*-(*p*-tolueneazo)methane, or. cryst. from C_6H_6, m.p. 159–160°.]

C̄ (1 mole) treated with aq. soln. of excess $NH_2OH.HCl$ (6 moles) + Na_2CO_3 (3 moles), stood 24 hrs., and acidified yields (15) methylglyoxal dioxime (methylglyoxime) [Beil. I-764, I_1-(396), I_2-(822)], pr. from alc. or aq., m.p. 157°, 153° (15) (30); the same prod. also results if a satd. soln. hydroxylamine sulfate is used (30) in place of free hydroxylamine.

C̄ (1 g.) in abs. alc. (20 g.) with phenylhydrazine (2.5 g.) stood for 1½ days, then warmed with aq. (100 ml.), yields (31) as insol. residue (1 g.) methylglyoxal *bis*-(phenyl)osazone [Beil. XV-156, XV_1-(38)], yel. ndls. from dil. alc., m.p. 148° (31).

Ⓓ **1,1-Dichloropropanone-2 semicarbazone:** m.p. 163° (32). [From C̄ in alc. with aq. semicarbazide.HCl (1 mole) without addn. of NaOAc, the semicarbazone pptg. immediately; note, however, that on stdg. the filtrate ppts. a small amt. of methylglyoxal *bis*-semicarbazone, m.p. 254°, also formed (together with equiv. C̄) on boilg. the semicarbazone with aq. (32).]

3:5430 (1) Cloëz, *Ann. chim* (6) **9**, 164–165, 175–176, 211–213 (1886). (2) Borsche, Fittig, *Ann.* **133**, 112–117, 124 (1865). (3) Cheng, *Z. physik. Chem.* **B-26**, 296 (1934). (4) Bell, Lidwell, *Proc. Roy. Soc. London*, **A-176**, 104–106 (1940). (5) Fittig, *Ann.* **110**, 38–43 (1859). (6) Harkins, Clark, Roberts, *J. Am. Chem. Soc.* **42**, 703 (1920). (7) Glutz, Fischer, *J. prakt. Chem.* (2) **4**, 53 (1871). (8) Mulder, *Ber.* **5**, 1007–1009 (1872). (9) Theegarten, *Ber.* **6**, 897–898 (1873). (10) Bischoff, *Ber* **8**, 1330–1336 (1875).

(11) Grabowski, *Ber.* **8**, 1438–1442 (1875). (12) Consortium fur Elektrochem. Ind , French 707,852, July 16, 1931; *Cent.* **1931**, II 2056. (13) Akashi, *Bull. Inst Phys -Chem. Research* 7 (1933). (14) Conrad, *Ann.* **186**, 882). (16) Buc (to Standard Oil 17) Wittorf, *J. Russ. Phys.-Chem. Soc.* **32**, 88–117 (1900); *Cent.* **1900**, II 29–30. (18) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1236 (1938); *Cent* **1939**, II 4223. (19) Dakin, *Biochem. J.* **11**, 91 (1917). (20) Nord, Ger. 434,728, Oct 5, 1926; *Cent.* **1926**, II 2845.

(21) Sen, *J. Indian Chem Soc.* **1**, 1–8 (1924/25), *Cent.* **1925**, I 537; *C.A.* **19**, 816 (1925); *Bio-* c **19**, 3277 (1925). (22) N. V. de Bataafsche F 1936; *Cent.* **1936**, II 865. (23) Linnemann, Z *Chem. Ztg.* **69**, 521 (1922). (25) Faworsky, *J. prakt Chem.* (2) **51**, 555–557 (1895). (26) Passerini, *Gazz. chim. ital* **54**, 540 (1924). (27) Wohl, *Ber.* **41**, 3605–3606 (1908). (28) Heller, Lauth, Buchwaldt, *Ber.* **55**, 485–486 (1922). (29) Favrel, *Bull. soc. chim.* (5) **1**, 988–989 (1934). (30) Treadwell, Westenberger, *Ber.* **15**, 2786–2787 (1882).

(31) Heller, *Ann.* **375**, 287–288 (1910). (32) Knöpfer, *Monatsh.* **32**, 765–766 (1911).

3:5450 1,3-DICHLOROPROPANE $ClCH_2.CH_2.CH_2Cl$ $C_3H_6Cl_2$ **Beil. I - 105**
(Trimethylene (di)chloride) I_1-(**34**)
I_2-(**73**)

B.P.		F.P.		
120.5–120.6° (1) (2) (3) (4)		**−99.5°** (8)	D_4^{25} = **1.1770** (11)	n_D^{25} = **1.4362** (12)
120.4°	at 760 mm. (5)			
	(6) (7)		$D_4^{17.6}$ = **1.1896** (13)	n_D^{20} = **1.452** (9)
120.3–120.5°	at 760 mm. (8)			**1.44867** (28)
120.2°	at 760 mm. (28)			
119.2°	at 740 mm. (9)			
119°	at 740 mm. (10)			

Colorless oil. — Note that b.p. of 125° given in I.C.T. is too high (4). — Almost insol. in aq. [for precise data see (1) (2) (3) (4)].

[For prepn. from propanediol-1,3 (trimethylene glycol) (1:6490) with fumg. HCl in s.t. at 100° (13) (10) (20–25% yield (14)) but always accompanied by 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) see indic. refs.; with $PCl_3 + ZnCl_2$ (21% yield (15)), or $PCl_5 + ZnCl_2$ (31% yield (15)), or $SOCl_2$ (50% yield (15)) see (15): for prepn. of C̄ from 1,3-dibromopropane (trimethylene dibromide) + $HgCl_2$ (8) (10) or 1,3-diiodopropane + AgCl (16) see indic. refs.: for prepn. of C̄ from γ-chloropropyl *p*-toluenesulfonate with various RMgX cpds see (12); for formn. of C̄ (19.3% (7) together with other products) by chlorination of propane (17) (18) (19) or *n*-propyl chloride (3:7040) (17) (18) see indic. refs.]

[C̄ with Zn dust in aq. alc. (20) (21) or better in a high-boilg. solvent (7) (22) yields cyclopropane, b.p. −34°.]

C̄ with alc. KOH yields allyl chloride (3:7035), b.p. 46°, which then reacts with the KOEt yielding (10) allyl ethyl ether (1:7850), b.p. 66–67° at 742 mm.

- Ⓓ **1,3-Diphenoxypropane** (1:7170) q.v.: lfts. from alc., m.p. 61° (23), 60–61° (24), 59–60° (25); b.p. 338–340° cor. at 762 mm. (26). [From C̄ (26) (or trimethylene dibromide (24) or trimethylene diiodide (25)) with sodium phenolate.]
- Ⓓ **1,3-Di-(α-naphthoxy)propane** [Beil. VI-607]: ndls. from alc., m.p. 103–104° (27).
- Ⓓ **1,3-Di-(β-naphthoxy)propane** [Beil. VI-642]: lfts. from AcOH, m.p. 148–149° (27).

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3:5460 TETRACHLOROETHYLENE (Perchloroethylene)

$Cl_2C{=}CCl_2$ C_2Cl_4 Beil. I - 187, I_1-(79), I_2-(161)

B.P.		F.P.		D		n	
121.20°	at 760 mm. (1)	−23.5°	(16)	D_4^{25} = 1.61463	(1)	n_D^{25} = 1.4993	(22)
121.1°	at 760 mm. (2)	−23°	(17)				
	(3) (4)						
121°	at 765 mm. (5)	−22.35°	(1)	D_4^{20} = 1.6230	(13)	n_D^{20} = 1.5058	(13)
121°	at 760 mm. (6)		(8)	1.623	(6)	1.50566	(2)
121°	(7)	−22.4°	(18)	1.62286	(1)	1.50547	(20)
120.8°	at 760 mm. (8)	−19°	(19)	1.6226	(20)		
120.74°	(9)			1.6207	(2)		
120.5–120.8°	at 770 mm. (10)						
119.5–120.5°	at 747 mm. (20)			D_4^{15} = 1.63109	(1)	n_D^{15} = 1.50812	(1)
119.0–120.0°	u.c. (11)			1.6230	(14)	1.50831	(1)
119–120°	at 753 mm. (12)					1.50899	(1)
118–120.5°	(13)						
118.5°	at 751 mm. (14)			$D^{12.5}$ = 1.6232	(21)		
118.0–118.1°	at 740 mm. (15)					$n_D^{12.5}$ = 1.5087	(21)
33.2°	at 30 mm. (14)			See also Note 2.			
See also Note 1.							

Note 1. For vap. press. of C̄ from 33–118° see (14). Note 2. For D_4^t over range t = 15–90° see (14).

Colorless liq. widely used as solvent, etc. (see also below). — $\bar{C}$ is pract. insol. aq., but detailed studies do not appear to be recorded. — $\bar{C}$ is miscible with alc., ether, $CHCl_3$, C_6H_6, and many other org. solvents.

GENERAL

[For study of $\bar{C}$ as solvent for detn. of mol. wts. by raising of b.p. (ebullioscopic const. = 55.0° per mole solute/100 g. $\bar{C}$) see (23). — For study of thermal conductivity see (24). — For soly. in $\bar{C}$ of gaseous HCl, H_2S, or NH_3 see (11). — For study of influence of $\bar{C}$ upon inflammability of mixts. of air with CH_4 (25) (10) (26) (27), with CO (10) (28), with H_2 (10), or acetylene (10) see indic refs.]

Binary systems contg. $\bar{C}$. [*System $\bar{C}$ + CCl_4*: for f.p./compn. data see (18); for n_D^{25}/compn. and use in anal. of the system see (22); for vap. press. and liq./vapor compn. of system see (29). — *System $\bar{C}$ + 1,1,2,2-tetrachloroethane* (3:5750): for f.p./compn. data see (17). — *System $\bar{C}$ + pentachloroethane* (3.5880): for f.p./compn. data (eutectic, f.p. −54 8° contg. 58.4 wt. % $\bar{C}$) see (18). — *System $\bar{C}$ + isopropyl alc.* (1:6135); for D_{25}^{25}/compn. and n_D^{25}/compn. data see (30)]

$\bar{C}$ forms binary azeotropes with many alcohols [e.g., *$\bar{C}$ with MeOH* (1:6120) forms a const-boilg. mixt, b.p 63.75° at 760 mm., contg. 36.5 wt. % $\bar{C}$ (3); *$\bar{C}$ with EtOH* (1:6130) forms a const.-boilg. mixt., b p. 76.75° at 760 mm., contg. 37 wt. % $\bar{C}$ (3); *$\bar{C}$ with n-propyl alc.* (1:6150) forms a const.-boilg. mixt., b.p. 94.05° at 760 mm., contg. 52 wt. % $\bar{C}$ (31); *$\bar{C}$ with isopropyl alc.* (1:6135) forms a const.-boilg. mixt., b.p. 81.7° at 760 mm., contg. 30 wt. % $\bar{C}$ (31), *$\bar{C}$ with n-butyl alc.* (1:6180) forms a const.-boilg. mixt., b.p. 108.95° at 760 mm., contg 71 wt. % $\bar{C}$ (3); *$\bar{C}$ with isoamyl alc.* (1:6200) forms a const.-boilg. mixt., b.p. 116.1° at 760 mm., contg. 80 wt. % $\bar{C}$ (31); *$\bar{C}$ with ethylene glycol* (1:6465) forms a const.-boilg mixt., b.p. 119.1° at 760 mm., contg. 94 wt. % $\bar{C}$].

$\bar{C}$ forms binary azeotropes with many other org. cpds. [e.g., *$\bar{C}$ with formic acid* (1:1005) forms a const-boilg. mixt., b.p. 88.15° at 760 mm., contg. 50 wt. % $\bar{C}$ (32); *$\bar{C}$ with AcOH* (1:1010) forms a const.-boilg. mixt., b p. 107.35° at 760 mm, contg. 61 5 wt. % $\bar{C}$ (218); *$\bar{C}$ with propionic acid* (1:1025) forms a const.-boilg. mixt., b.p. 119 15° at 760 mm., contg. 91.5 wt % $\bar{C}$ (4); *$\bar{C}$ with isobutyric acid* (1:1030) forms a const.-boilg. mixt., b.p. 120.5°, contg. 97 wt. % $\bar{C}$ (33)]

Uses of $\bar{C}$. $\bar{C}$ because of its solvent properties, b.p., uninflammability, and immiscibility with aq., etc., finds wide use. — [Other examples of its utility include the following: for use as dry-cleaning solvent see (34), cf. (35) (36) (222); for use with lower aliph. alcs. as solv. for cellulose ethers see (37); for use in dewaxing of lubricating oil see (38); for use in liq. HCN to diminish inflammability and explosiveness see (39); for use as a component of comml. tear-gas mixts. see (40).]

[For study of use of $\bar{C}$ as an anesthetic (41), as fumigation agt. (with CCl_4) for grain or flour (42), for sterilization of surgical catgut (43), of antiseptic action (compared with $CHCl_3$ (44)) (45) see indic. refs.]

[For examples of studies of use of $\bar{C}$ as anthelmintic especially with reference to hookworm and similar parasites see (46)-(57) incl.; for comparison of anthelmintic action of $\bar{C}$ with that of CCl_4 (58) (59) or of chenopodium oil (60) see indic. refs.; for patent prepn. of $\bar{C}$ for use as anthelmintic see (61).] (For toxicity see below.)

[For use of $\bar{C}$ as the "booster" liquid in detn. of aq. by distn. especially in molasses and other sugar industry products see (62) (63) (64) (65) (66) (67). — For use of $\bar{C}$ in prepn. of anhydrous Na_2O_2 by removal of moisture by distn. see (68).]

[For brief general surveys of $\bar{C}$ see (69) (70).]

Physiological actn. and/or toxicity of $\bar{C}$. [For studies from various viewpoints on toxicity of $\bar{C}$ see (57), (71)-(82) incl., also especially (219) (220) (224).]

Determination of $\bar{C}$. $\bar{C}$ is usually detd. by some form of decn. followed by volumetric or gravimetric detn. of resultant chloride ion [e.g., for methods involving decn. of $\bar{C}$ with Na + AmOH in xylene (83) (84), with Na + ethanolamine in dioxane soln. (85) (223), or with Na in liq. NH_3 (86) (note that some cyanide formn. occurs) see indic. refs.; for methods involving thermal decn. see (87) (215)].

[For detn. of $\bar{C}$ by means of a recording ultra-violet photometer (the R. + H. Tri-Per Analyzer) see (88).]

PREPARATION OF $\bar{C}$

From various polychloroethanes or polychloroethylenes. [For prepn. of $\bar{C}$ from hexachloroethane (3:4835) by pyrolysis at 565° (89–94% conversion (89)), by passing over porcelain chips in hot tube (90) (note that CCl_4 (3:5100) is also formed), or by passing with H_2 over Ni at 270° (91) see indic. refs.; for prepn. of $\bar{C}$ from hexachloroethane (3:4835) by treatment with granulated Zn in boilg. alc. (7), with Zn + dil. H_2SO_4 at room temp. for several days (100% yield (5)) (92) (116), or even with Zn + aq. above 80° (93), with alc. KSH (94), with molecular Ag at 280° in s.t. (95), with SbF_3 at 300–325° under press. (96), with acetylene over activated carbon at 200–400° (97) cf. (123), with aniline at 170° at ord. press. (7), with N/10 abs. EtOH/NaOH at 25° (216), or with alc. free NaOEt in ether under press. at 140° (217) see indic. refs.]

[For prepn. of $\bar{C}$ from pentachloroethane (3:5880) by elimination of 1 HCl in various ways: e.g., by passing over bone char at 280° (98), or over $NiCl_2$ at 330° (99), by htg. with $AlCl_3$ at 70–100° (100% yield (101)) (100) or under reflux (102), with liq. NH_3 at −18 to −34° under reduced press. (103) (104), with MeOH over Al_2O_3 at 290° (MeCl (3:7005) is also formed) (105), with acetylene over cat. at 200–300° (vinyl chloride (3:7010) is also formed) (106), with alc. KOH (107) (108), or in alc. with 2 N aq. NaOH in cold (98% yield) (109) see indic. refs.]

[For prepn. of $\bar{C}$ from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) (see also below under prepn. of $\bar{C}$ from acetylene) on pyrolysis at 700° (110), with air over pumice + $CuCl_2$ at 430–450° (111), or with Cl_2 over activated carbon contg. 80% $CuCl_2$ at 300–320° (112) see indic. refs.]

[For prepn. of $\bar{C}$ from 1,2-dichloroethane (ethylene dichloride) (3:5130) with Cl_2 over cat. at 300–500° see (113); from ethane or its chloro derivs. with Cl_2 + fused metal chlorides such as $AlCl_3$, etc., at 250–500° see (114).]

[For formn. of $\bar{C}$ from trichloroethylene (3:5170) on pyrolysis at 700° (110) or with anhyd. $FeCl_3$ on htg. see (115).]

From various polychloromethanes. [For prepn. of $\bar{C}$ from CCl_4 (3:5100) through tube at 1300–1400° see (116) (117); for formn. of $\bar{C}$ (together with other prods.) from CCl_4 + H_2 through hot tube over pumice at low red heat (118) or through tube at 600–650° (119), or in dark electric discharge (120), see indic. refs. — Note also that $\bar{C}$ has been found (121) as a by-prod. of prepn. of CCl_4 (3:5100) by actn. of Cl_2 on CS_2.]

[For formn. of $\bar{C}$ from $CHCl_3$ (3:5050) + H_2 in dark electric discharge see (120).]

From acetylene with Cl_2 (see also above under prepn. of $\bar{C}$ from 1,1,2,2-tetrachloroethane (acetylene tetrachloride)). [For prepn. of $\bar{C}$ from acetylene with Cl_2 + inert gas over cat. at 250–400° see (122) (123) (124) (125); from acetylene with Cl_2 at 700–900° in absence of extraneous substances (126); from acetylene with Cl_2 see (127) (128); from acetylene with Cl_2 in halogenated solv. at 175–260° + $AlCl_3$, etc., see (129).]

From miscellaneous sources. [For prepn. of $\bar{C}$ from CO + HCl over cat. at 230–240° under high press. ($CHCl_3$ is also formed) see (130); from *unsym.*-heptachloropropane (3:0200) by dissociation into $\bar{C}$ + $CHCl_3$ over Cu_2Cl_2 at 250° see (131); from chloral (3:5210) by long boilg. with $AlCl_3$ see (132) cf. (133) (134); from tetrachloroethyl chloro-

formate with $AlCl_3$ see (135); from trichloroacetic acid (3:1150) over ThO_2 + kaolin at 230–250° see (136); from pentachloropropionic acid (3:4895) on htg. in aq. (137), or from its ferric salt in light (139) cf. (140), or from pentachloropropionyl chloride (3:0470) with $AlCl_3$ (1 mole) at 60° (138) see indic. refs.]

PURIFICATION OF $\bar{C}$

Comml. $\bar{C}$ conts. some impurity which readily chlorinates (15); note also that $\bar{C}$, especially if exposed to light and air, may contain phosgene (3:5000), trichloroacetyl chloride (3:5420), trichloroacetic acid (3:1150), and other prods.; cf. below under oxidation of $\bar{C}$. — [For purification of $\bar{C}$ by treatment with Cl_2 followed by illumination (15), by treatment with aq. alk. at elev. temp. (for removal of 1,1,2-trichloroethane (3:5330) or 1,1,1,2-tetrachloroethane (3:5555)) (141), by refluxing with finely divided metals + dil. acid (142) or with 1% Al or $AlCl_3$ (143), or by passing vapor over kaolin at 250° (144), see indic. refs.]

STABILIZATION OF $\bar{C}$

To increase the resistance of $\bar{C}$ to photooxidation (see below) and other changes, the addition of very small amts. of various stabilizers has been recommended. — [For example, for study of control of photooxidation of $\bar{C}$ by use of inhibitors such as thymol (1:1430), ether, alcohol, thiourea, etc., see (145). — For stabilization of $\bar{C}$ by addn. of small amts. of paraffin hydrocarbons (e.g., gasoline) (146), various phenols (such as hydroquinone monomethyl or monobenzyl ether) (147), oil-sol. azo dyes contg. phenolic groups (148), mercaptans (such as n-butyl mercaptan) (149), various org. tertiary amines such as triethylamine (150) or picoline (151), various phenols, amines, and aminophenols (152), or a wide variety of org. N cpds. (221) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis. [$\bar{C}$ on pyrolysis over heated Pt wire gives (153) (154) hexachloroethane (3:4835) + hexachlorobenzene (3:4939) + Cl_2.]

Hydrogenation. [Note that $\bar{C}$ does not add H_2 even in pres. of Ni at 300–350° (99); $\bar{C}$ with excess H_2 over Ni at 220° dec. (163) to carbon + HCl.]

Oxidation. $\bar{C}$ can be oxidized especially in the presence of light and moisture giving according to conditions trichloroacetyl chloride (3:5420), phosgene (3:5000), trichloroacetic acid (3:1150), or various mixtures of these prods.; for inhibition of this oxidation see above under stabilization of $\bar{C}$

[For extensive studies of photochem. oxidn. of $\bar{C}$ giving 87% trichloroacetyl chloride accompanied by phosgene see (15) (155) (156); for oxidn. of $\bar{C}$ on stdg. with aq. in light for 4 months yielding trichloroacetic acid see (157) cf. (158); for oxidn. of $\bar{C}$ to trichloroacetyl chloride with O_3 (159) (160), with peracetic acid (acetyl hydrogen peroxide) (161), with conc. HNO_3 + conc. H_2SO_4 in freezing mixt. (162), with SO_3 at 150° (164), or with N_2O_5 (194) see indic. refs.; for patents on photochem. oxidn. of $\bar{C}$ to trichloroacetyl chloride (3:5420) see (165) (166).]

[$\bar{C}$ on oxidn. with $K_2Cr_2O_7/H_2SO_4$ is completely converted to CO_2 + H_2O + HCl (167); $\bar{C}$ passed with air over CuO at 450° gives only traces (168) of phosgene.]

Reaction with halogens. [$\bar{C}$ dislvd. in dichlorodifluoromethane ("Freon") with F_2 at −80° (169), or $\bar{C}$ with F_2 at 0° directly (170) but *not* in CCl_4 soln. (169) cf. (172), or $\bar{C}$ in vapor phase at 130° with F_2 diluted with N_2 (171), gives (20% yield (171)) 1,2-difluoro-1,1,2,2-tetrachloroethane, m.p. 26.5° (96) (169), accompanied by various other prods. such as fluoropentachloroethane, m.p. 99.0–99.5° (in s.t.), b.p. 136–138° (170), and 1,4-difluoro-octachlorobutane (170) (169), m.p. 4–5° (170), b.p. 152.2° at 20 mm., D_4^{20} = 1.9272, n_D^{20} = 1.5256 (170).]

[$\bar{C}$ with dry Cl_2 in direct sunlight (90), or $\bar{C}$ in CCl_4 at 22° (173) or in vapor phase at 40° and low press. (155) in light and absence of O_2, or $\bar{C}$ with SO_2Cl_2 in pres. of dibenzoyl peroxide (174) *adds* Cl_2 yielding hexachloroethane (3:4835) q.v.; note, however, that $\bar{C}$ + Cl_2 + light in pres. of O_2 undergoes photooxidation to trichloroacetyl chloride (see above under oxidation of $\bar{C}$). — $\bar{C}$ with Cl_2 at 700–800° (175), or $\bar{C}$ with Cl_2 over act. carbon at 600–650° (176), undergoes cleavage of C—C bond yielding CCl_4 (3:5100); for study of this reactn. see (177).]

[$\bar{C}$ with Br_2 in sunlight adds 1 mole Br_2 yielding (178) (179) (110) 1,2-dibromo-1,1,2,2-tetrachloroethane, m.p. 197.5° dec. (in s. cap. tube) (180), 200–205° dec. (110), 190° dec. (138). — Note, however, that this photochem. addn. is inhibited by its reactn. prod. (181), that, although accelerated by *small* amts. O_2, pres. of large amts. O_2 lead to a halogen catalyzed photooxidation (181), that in CCl_4 soln. resultant equilibrium mixt. conts. only 30% addn. prod. (182). — For extensive study of this reactn. see (181); for studies of its rate see (183) (184); for extensive study of photochem. dissoc. of prod. see (179). — For study of reactn. of $\bar{C}$ with radio-bromine see (185).]

[$\bar{C}$ does not add I_2. — For soly. of I_2 in $\bar{C}$ see (186); for use of such solns. in detn. of iodine number of unsatd. oils and fats see (187) (188).]

Behavior of $\bar{C}$ with other inorganic materials. [$\bar{C}$ with Cl_2O in CCl_4 at −20° gives (189) hexachloroethane (3:4835).]

[$\bar{C}$ with NO_2 in s.t. at 100–120° for 3 hrs. (190), or at 100–110° for 3 hrs. (5), or at 80° for 3 hrs. or 60° for 6 hrs. (191), or at 10–12 atm. press. at 60–80° for 3–6 hrs. (191), or $\bar{C}$ with fumg. HNO_3 at ord. temp. stood several days (5) cf. (192), adds 2 moles NO_2 yielding 1,2-dinitro-1,1,2,2-tetrachloroethane [Beil. I-102, I_1-(33)], cryst. from alc., m.p. 142–143° (s. cap. tube) (5).]

[$\bar{C}$ with nitryl chloride ($ClNO_2$) yields (193) 1-nitro-1,1,2,2,2-pentachloroethane, lfts. from alc., m.p. 192° (s. cap. tube) (193).]

[$\bar{C}$ with N_2O_5 undergoes vigorous oxidn. (presumably to trichloroacetyl chloride) (194).]

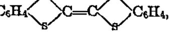
[$\bar{C}$ with NH_3 at 700–800° splits off all its halogen as NH_4Cl (195) cf. (196).]

[For behavior of $\bar{C}$ with various common metals see (197); note that $\bar{C}$ is not attacked by molecular Ag even at 300° (95); note that $\bar{C}$ with Na or K or their mixture may (like many other polychloro compds.) explode under certain conditions (for an extensive study see (198)).]

Behavior of $\bar{C}$ with organic reactants. [$\bar{C}$ (1 mole) with $CHCl_3$ (2 moles) + $AlCl_3$ (0.2 mole) refluxed 15–20 hrs. gives (85–93% yield (199)) (101) (16) (200) (201) (202) (214) *unsym.*-heptachloropropane (3:0200); for study of equilibrium of system $\bar{C}$ + $CHCl_3$ + *unsym.*-heptachloropropane see (131).]

[$\bar{C}$ with 1,1,2,3,3-pentachloropropene-1 (3:6075) + $AlCl_3$ gives (201) cf. (214) 1,1,3,4,5,5,6,6,6-nonachloropentene-1.]

[$\bar{C}$ with NaOEt at 100–120° yields (203) ethyl dichloroacetate (3:5850) + Na diethoxyacetate + other prods., presumably via ethyl α,β,β-trichlorovinyl ether, α,α-dichloro-β,β-diethoxyethylene, triethyl dichloroorthoacetate, etc., cf. (204).]

[$\bar{C}$ (1 mole) with $NaSC_6H_5$ (2 moles) in alc., refluxed 48 hrs., gives (yield not stated (205)) α,β-dichloro-α,β-*bis*-(thiophenyl)ethylene, ndls. from alc., m.p. 71–72° (205). — $\bar{C}$ with disodium salt of dithiopyrocatechol in alc. at 110–120° in s.t. for 7 hrs. gives small yield (206) of , golden ndls., m.p. 234° (206).]

[$\bar{C}$ with paraformaldehyde (1:0080) + conc. H_2SO_4 as directed (207) gives α,α-dichloro-β-hydroxypropionic acid, m.p. 88–89° (s. cap. tube).]

[$\bar{C}$ with dibenzoyl peroxide on refluxing either with or without $AlCl_3$ gives (40% yield

(208)) α,α,β-trichloro-β-phenylethylene (α,α,β-trichlorostyrene) [Beil. V-477, V_2-(367)], b.p. 87–89° at 3 mm., $D_-^{25} = 1.40$, $n_D^{25} = 1.5758$ (208), accompanied by chlorobenzene (3:7903), CO_2, and under certain conditions by hexachloroethane (3:4835).]

[$\bar{C}$ with large excess EtMgBr in boilg. ether evolves ethylene and on subsequent treatment with aq. gives a mixt. of ethylene + acetylene; for explanation see (209). — $\bar{C}$ with n-butyllithium in pet. eth. gives violent explosion (210).]

[For study of reactn. of $\bar{C}$ with pyridine or piperidine at 16–18° see (211).]

Ⓟ Color test with NH_4OH/Cu_2Cl_2: $\bar{C}$ (1–2 drops) in small glass-stoppered bottle filled with conc. aq. NH_4OH, treated with powdered Cu_2Cl_2, stopper quickly inserted (to force out air and excess liquid), shaken, and allowed to stand, gives in 3 days a pale amethyst color (212); note, however, that $\bar{C}$ on stdg. with metallic Cu + conc. aq. NH_4OH develops rich port-wine red color in aq. layer and brown coating on the copper (213). — Note also that neither of these tests should be regarded as conclusive (see (212) (213)).

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Sci. Fennicae,
(1928) (24)
nes, *Ind. Eng.*
(1924). (27)
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(30) Bergelin,

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(35) Brown,
urists **50**, 72–76 (1934).
nt. **1923**, IV 164. (38)
1936, I 2672; *C.A.* **30**,
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122, April 4, 1922; *Cent.*

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Ortlepp, *Onderstepoort*
tlepp, Mönnig, *Onderste-*
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(151) Crawford, Duncan, & Imperial Chem. Ind, Ltd., Brit. 493,875, Nov. 10, 1938, *Cent.* **1939**, I 1252, *C A* **33**, 2540 (1939). (152) Roessler & Hasslacher Chem Co, French 732,569, Sept 22, 1932, *Cent* **1932**, II 3785, *C A.* **27**, 304 (1933), Ger. 573,105, March 3, 1932; *C.A.* **27**, 2961 (1933). (153) Lob, *Z. Elektrochem* **7**, 903–921 (1901); *Cent* **1901**, II 1042. (154) Joist, Löb, *Z Elektrochem.* **11**, 938–944 (1905), *Cent* **1906**, I 223. (155) Dickinson, Carrico, *J. Am. Chem. Soc* **56**, 1473–1480 (1934). (156) Muller, Ehrmann, *Ber* **69**, 2207–2210 (1936). (157) Bailey, Hickson, *J Chem. Soc.* **1941**, 145 (158) Kobe, *Ann.* **54**, 182 (1845). (159) Besson, *Compt rend* **118**, 1347 (1894), *Bull. soc chim.* (3) **11**, 918–919 (1894). (160) Swarts, *Bull. acad. roy Belg* (3) **36**, 532–552 (1898); *Cent.* **1898**, I 588–589.

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(191) Argo, James, Donnelly, *J. Phys. Chem.* **23**, 578–585 (1919). (192) Burrows, Hunter, *J. Chem. Soc.* **1932**, 1357–1360. (193) Steinkopf, Kühnel, *Ber.* **75**, 1327 (1942). (194) Haines, Adkins, *J. Am. Chem. Soc.* **47**, 1422–1423 (1925). (195) Heslinga, *Rec. trav. chim.* **43**, 179 (1924). (196) Stähler, *Ber.* **47**, 912 (1914). (197) Gowing-Scopes, Analyst **39**, 7 (1914). (198) Lenze, *Z. ges. Schiess- u. Sprengstoffw.* **27**, 255–258, 293–296, 337–340, 373–376 (1932); *Cent.* **1933**, I 1716; *C.A.* **27**, 844 (1933). (199) Farlow, *Org. Syntheses*, Coll. Vol. **2** (1st ed.), 312–313 (1943); **17**, 58–59 (1937). (200) Henne, Ladd, *J. Am. Chem. Soc.* **60**, 2494 (1938).

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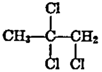
(221) Missbach (to Stauffer Chem. Co.), U.S. 2,043,257–2,043,260 incl., June 9, 1936; *Cent.* **1936**, II 3845; *C.A.* **30**, 5240 (1936). (222) Grebe, Stoesser, Mills (to Dow Chem. Co), U.S. 1,989,478, Jan. 29, 1935; *Cent.* **1935**, II 3859; *C.A.* **29**, 2000 (1935). (223) Rauscher, *Ind. Eng. Chem. Anal. Ed.* **9**, 296–299 (1937). (224) Lehman, Schmidt-Kehl, *Arch. Hyg. Bakt.* **116**, 131–268 (1936); *C.A.* **31**, 477 (1937).

3:5475 1,2,2-TRICHLOROPROPANE



$C_3H_5Cl_3$ Beil. I - 106 I_1— I_2—

B.P. 123° (1) (2)
123–125° (3)

$D^{25}_{25} = $ **1.318**

[For prepn. as a by-product of the chlorination of propane see (2); for formn. of $\bar{C}$ (47%) in chlorination of 1,2-dichloropropane (3:5200) see (3).]

$\bar{C}$ with alc. KOH splits out HCl and gives two stereoisomeric 1,2-dichloropropenes, viz., 3:5110 and 3:5150.

3:5475 (1) Herzfelder, *Ber.* **26**, 2435 (1893). (2) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935; *Cent.* **1935**, I 1500. (3) Zellner (to Tide Water Associated Oil Co.), U.S. 2,370,342, Feb. 27, 1945, *C.A.* **39**, 3534 (1945).

CHAPTER XIII

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:5500–3:5999)

3:5500 *cis*-2,3-DICHLOROBUTENE-2 $C_4H_6Cl_2$ Beil. S.N. 11

Cl Cl
CH_3—C=C—CH_3

B.P. 124–126° at 758 mm. (1)	D_4^{20} = 1.1618 (1)	n_D^{20} = 1.4590 (1)
	D_4^{18} = 1.1620 (1)	n_C^{18} = 1.4616 (1)

[*See also trans stereoisomer* (3·7395).]

[For prepn. of $\bar{C}$ (accompanied by its *trans* stereoisomer (3:7395)) from 2,2,3-trichlorobutane (3:5680) with solid KOH (1 mole) at 135–140° see (1).]

$\bar{C}$ on oxidn. with 3% aq. $KMnO_4$ yields (1) acetic acid (1:1010).

$\bar{C}$ in CCl_4 at −20° treated with 7% O_3, then hydrolyzed, yields (1) acetic acid (1:1010) + acetaldehyde (1:0100).

3:5500 (1) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) 6, 1553–1558 (1936); *Cent.* 1937, I 3785; *C.A.* 31, 2165 (1937).

3:5515 TRICHLOROMETHYL CHLOROFORMATE $C_2O_2Cl_4$ Beil. III - 18

[illegible].O.CO.Cl III₁-(8)

[illegible] III_2-(16)

B.P.			M.P.		
127.5–128° (1) cor.		(2)	−57°	D_{21}^{21} = 1.632 (7)	n_D^{26} = 1.456 (1)
127°	at 760 mm.	(3)			
126–127°	at 745 mm.	(4)		D_{15}^{15} = 1.655 (3)	n_D^{22} = 1.45664 (8)
		(5)			
127.2°	at 725 mm.	(6)			
49°	at 50 mm.	(3)			
45°	at 26 mm.	(7)			
20°	at 10.3 mm.	(1)			
0°	at 2–4 mm.	(1)			

Colorless oily liq. with irritating and suffocating odor, but (when pure) not especially lachrymatory. — Ord. samples may cont. triphosgene (3:1915).

[For prepn. from methyl formate (1:1000) or methyl chloroformate (3:5075) by chlorination see (8) (3) (9) (2) (1); for prepn. from *bis*-(trichloromethyl) carbonate (triphosgene) (3:1915) see (1); for German prepn. in World War I see (10).]

$\bar{C}$ (when pure) boils with no decompn. (1); however, above 300° (2) or on contact with activated carbon, charcoal, or iron oxide at ord. temp. (1) $\bar{C}$ decomposes to phosgene

(3:5000). — $\bar{C}$ on contact with alumina (1), $AlCl_3$ (5), or $FeCl_3$ (3) decomposes in a different mode yielding CCl_4 (3:5100) + CO_2.

$\bar{C}$ with aq. hydrolyzes slowly in the cold but rapidly at 100° yielding only HCl + CO_2 (1) (3); $\bar{C}$ on warming with aq. Na_2CO_3 yields NaCl + CO_2 (3).

$\bar{C}$ on treatment at 20° for 5 min. with NaI in acetone evolves CO and separates I_2 to 98.8% of amt. expressed by reaction: $Cl_3C.O.CO.Cl + 2NaI \rightarrow 2CO + 4NaCl + I_2$ (11) [cf. chloromethyl chloroformate (3:5275), dichloromethyl chloroformate (3:5315), and triphosgene (3:1915)].

$\bar{C}$ with aq. NH_4OH reacts vigorously yielding urea + NH_4Cl. — $\bar{C}$ with excess aniline in either aq. or non.-aq. soln. is converted to *N,N'*-diphenylurea (carbanilide), m.p. 233°, + aniline hydrochloride (3). [Note that with insufficient aniline a mixt. of phenyl isocyanate + *N*-phenylcarbamyl chloride may form (3).]

$\bar{C}$ on addn. in cold to conc. soln. of phenol (1 mole) in aq. NaOH separates an oil (which soon solidifies) of phenyl trichloromethyl carbonate [Beil. VI_1-(88)], ndls. from ether, m.p. 70.5° (12), 66° (3); this product upon warming with aq. sodium phenolate (or $\bar{C}$ warmed with excess sodium phenolate in one operation) yields diphenyl carbonate (1:2335), cryst. from alc., m.p. 78° (12). [For corresponding reactions with *p*-cresol (1:1410), *β*-naphthol (1:1540), *p*-chlorophenol (3:0475), and *p*-nitrophenol see (13).]

$\bar{C}$ with pyridine yields a yel. double quaternary ammonium salt $C_5H_5N(Cl).CO(Cl)$-$N.C_5H_5$ which by aq. is decomposed to pyridine hydrochloride + CO_2 (14).

[For use of $\bar{C}$ in prepn. of acid chlorides of carboxylic or sulfonic acids see (15); similarly $\bar{C}$ htd. with anhydrous NaOAc gives Ac_2O + NaCl + CO_2 (2); for actn. on methyl hydrogen sulfate yielding methyl chlorosulfonate + phosgene + CO_2 see (16).]

[For use of $\bar{C}$ for introduction of a second —CO.Cl group into acid chlorides see (17).]

514 (1919). (2) Hentschel, *J. prakt. Chem.*
Schmitz, *Ann. chim.* (9) **13**, 44–49 (1920).
-96 (1930). (5) Ramsperger, Waddington,
r, *Helv. Chim. Acta* **21**, 788 (1938). (7)
) Grignard, Rivat, Urbain, *Ann. chim.* (9)
(2) **36**, 209–215 (1887). (10) Norris, *Ind.*
6); *C.A.* **30**, 7423 (1936). (12) Ref. 4, pp
235 (1930). (14) Ger. 109,933, May 27, 1898; *Cent.* **1900**, II 460. (15) Brit. 401,643, Dec. 14, 1933; *Cent.* **1934**, II 2133. (16) Kraft, Alekseev, *J. Gen. Chem.* (*U.S.S.R.*) **2**, 726–729 (1932); *C.A.* **27**, 2426 (1933); *Cent.* **1933**, II 1666. (17) Kharasch, Eberly, Kleiman, *J. Am. Chem. Soc.* **64**, 2975–2977 (1942).

3:5540 **α,β-DICHLOROVINYL ETHYL ETHER** $C_4H_6OCl_2$ **Beil. I - 724**
(α,β-Dichloro-α-ethoxyethylene) **I_1-(377)**
I_2-(780)

$$\underset{Cl}{CH}=\underset{Cl}{CH}—O—CH_2CH_3$$

B.P. **128.2°** cor. (1)	D_4^{25} = **1.1972** (3)
125–127° (4)	D_4^{20} = **1.2037** (3)
122–126° (2)	$n_D^{16.5}$ = **1.45584** (3)

$\bar{C}$ has the possibility of existing in two geometrically isomeric forms, but only this one has as yet been recognized.

[For prepn. of $\bar{C}$ from trichloroethylene (3:5170) with alc. KOH (4), with alc. NaOEt (yield: 81% (5), 70% (2)), or with alc. NaOH + CaO (6) see indic. refs.; from 1,1,1,2-tetrachloroethane (3:5555) with NaOEt see (1).]

[$\bar{C}$ with calcd. amt. aq. (7), or with conc. HCl (8) yields ethyl chloroacetate (3:5700);

$\bar{C}$ on boilg. with aq. to complete soln. yields (9) chloroacetic acid (3:1370); $\bar{C}$ on htg. with aq. in s.t. at 180° yields (1) glycolic acid (1:0430), EtCl (3:7015) + HCl.]

[$\bar{C}$ with HCl gas yields (10) an addn. prod. which on htg. decomposes to chloroacetyl chloride (3:5235) + EtCl (3:7015); $\bar{C}$ with monobasic org. acids yields (2) on htg. ethyl chloroacetate (3:5700) + corresp. acid chloride; with succinic acid the products are (2) ethyl chloroacetate (3:5700) + succinic anhydride (1:0710).]

[$\bar{C}$ with alcohols yields mainly (2) (11) the corresp. alkyl chloroacetate + EtCl (some ethyl chloroacetate + alkyl chloride are also formed (2)); $\bar{C}$ htd. with excess NaOEt yields (1) sodium salt of ethoxyacetic acid (1:1070).]

[$\bar{C}$ with phenols yields exclusively (2) the corresp. aryl chloroacetate + EtCl; e g., $\bar{C}$ with β-naphthol (1:1540) yields (2) β-naphthyl chloroacetate, m.p. 95° (2).]

$\bar{C}$ with aniline in aq. or aq. alc. soln. yields (12) ethyl N-phenylaminoacetate (90%) [Beil. XII-470, XII_1-(263)], m.p. 58°, and phenylaminoacetanilide (10%) [Beil. XII-556, XII_1-(285)], m.p. 112°

[$\bar{C}$ readily absorbs Cl_2 at ord. temp.; if moisture is carefully excluded, the prod. breaks up (13) (14) *on keeping or on htg. into dichloroacetyl chloride* (3:5290) + EtCl (3:7015); if, however, moisture is given access or aq. added, then on keeping or htg. the prod. breaks up (13) (14) and on distn. gives alm. theoretical yield of ethyl dichloroacetate (3:5850) + HCl.]

[$\bar{C}$ readily absorbs Br_2; with complete exclusion of aq. the products are (13) (14) bromo-chloro-acetyl chloride, b.p. 138–139° (13), and EtBr; in pres. of aq. the products are ethyl chloro-bromo-acetate, b.p. 174°, D_4^{22} = 1.5890 (13), + HCl + HBr; some bromo-chloro-acetyl *bromide*, b.p. 158–160°, 47–49° at 15 mm. (15), and C_2H_5Cl (3:7015) are also (15) formed. — $\bar{C}$ on treatment with Br_2 in the cold, then immediately followed by alc. KOH, gives good yield (3) of β-bromo-α,β-dichlorovinyl ethyl ether, b.p. 177° at 754 mm., D_4^{20} = 1.6565, n_D^{17} = 1.50427 (3).]

[$\bar{C}$ treated with ICl, stood 30 min. (17), filtered from I_2, then htd. to 50° to expel C_2H_5Cl gives (16) (17) chloro-iodo-acetyl chloride; addn. of aq. to latter yields by hydrolysis (16) (17) chloro-iodo-acetic acid, colorless lfts from lt. pet., m.p. 90° (16).]

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(11) Imbert, Consortium für Elektrochem. Ind., Ger. 212,592, Sept 6, 1909; *Cent.* **1909**, I 1021. (12) Imbert, Consortium für Elektrochem. Ind , Ger. 199,624, June 24, 1908, *Cent.* **1908**, II 358. (13) Crompton, Triffitt, *J. Chem Soc.* **119**, 1874–1875. (14) McKie, *J. Chem. Soc.* **123**, 2213–2217 (1923). (15) Backer, Mook, *J. Chem Soc.* **1928**, 2126. (16) Crompton, Carter, *J. Chem. Soc.* **123**, 576–577 (1923). (17) McMath, Read, *J. Chem. Soc.* **1927**, 538–539.

n_D^{25} see (10). — $\bar{C}$ with *di-n-butyl ether* (1:7350): for b.p., vapor-liq. equil. [illegible] — $\bar{C}$ with *β,β'-dichloro-diethyl ether* (3:6225): for b.p., vapor-liq. equil. [illegible] (see below under azeotropes).

$\bar{C}$ with chlorinated hydrocarbons. $\bar{C}$ with *1,2-dichloroethane* [illegible] (3:5130): for b.p., vapor-liq. equil., and *D* see (31) (see also [illegible]) (For use of ethylene dichloride in dehydration of $\bar{C}$ see (32).)

Azeotropes Containing $\bar{C}$

Binary azeotropes. $\bar{C}$ with water forms a const.-boil. mixt. b.p. [illegible] (26) (8), 97.8° at 760 mm. (23) (32), contg. 45.8 wt. % [illegible] (32) $\bar{C}$: constants for this azeotropic mixt. at other press. include the following: b.p. 96–96.2° (26); at 735 mm., b.p. = 95.8° (33) (11), [illegible] at 504 mm., b.p. = 86.4° (23); at 400 mm., b.p. = 80.35°, [illegible] Note that compn. changes only slightly (23) with press. — For study [illegible] (11) (23) or of HCl (11) see indiv. refs.

$\bar{C}$ with *toluene* (1:7405) gives a const.-boil. mixt., b.p. [illegible] (10). — $\bar{C}$ with *di-n-butyl ether* (1:7350) gives a const.-boil. mixt., b.p. [illegible] 68 mole % $\bar{C}$ (10). — $\bar{C}$ with *β,β'-dichlorodiethyl ether* (3:6225) gives a mixt. b.p. 128.2°, contg. 91.8 mole % $\bar{C}$ (10).

Ternary azeotropes: $\bar{C}$ with aq. + C_6H_6 (1:7400) gives a const.-boil. [illegible] 67.0–67.3° (29). — $\bar{C}$ with aq. + ethylene dichloride (3:5130) gives a [illegible] b.p. 69.6° (29). — $\bar{C}$ with aq. + 1,1,2-trichloroethylene (3:5170) gives [illegible] mixt., b.p. 70.8–71.5° (29).

Miscellaneous Physical Properties of $\bar{C}$

[For sepn. of $\bar{C}$ from gas mixts. by adsorption (?) on $Mg(ClO_4)_2$ [illegible] see (34).]

Uses of $\bar{C}$

The manifold uses of $\bar{C}$, based upon both its physical and its chemical [illegible] cannot here be reviewed in detail; however, some examples include the following:

[For use in sepn. of butadiene from hydrocarbon mixts. (35), in [illegible] naphthenes from mineral lubricating oils (36), in refining of rosin (37) [illegible] pine lignin (38) (39), as solv. for various resins (40), as solv. for cellulose [illegible] cellulose ethers (42), for addn. to rayon spinning baths (43) see indiv. refs.]

Physiological and Biochem. Behavior of $\bar{C}$

[For study of pharmacol. of $\bar{C}$ (or its phosphoric esters, etc.) see (44); [illegible] poisoning by $\bar{C}$ see (45) (46); for study of toxicity of vapor of $\bar{C}$ see (46).]

[For effect of $\bar{C}$ upon amylase (47) (48) or lipase (49) see indiv. refs.; for [illegible] of yeast of depressed enzymatic activity see (50).]

Determination of $\bar{C}$

[For colorimetric detn. of $\bar{C}$ by reactn. with diazotized sulfanilic acid [illegible] 25° see (103) (note that method involves oxidn. of $\bar{C}$ by the reagt. to chloro[illegible] (3:7212) and color formn. with latter); for detn. of $\bar{C}$ in aq. solns. by [illegible] (11) (23) (8) (25).]

3:5552 2-CHLOROETHANOL-1 (Ethylene chlorohydrin, β-chloroethanol, β-chloroethyl alcohol, " glycol chlorohydrin ") $\underset{Cl}{\underset{|}{CH_2}}—CH_2OH$ C_2H_5OCl Beil. I - 337, I_1-(170), I_2-(333)

B.P.	F.P.	D	n_D
[132° at 761 mm. (1)]	−67.5° (7)	D_4^{25} = 1.1972 (14)	n_D^{25} = 1.44123 (22)
[132.0° (2)]	(8)	1.19654 (8)	1.4412 (18)
[130-131° at 760 mm. (3)]	−69.0° (21)	1.1961 (10)	1.44012 (9)
		1.1947 (9)	
129.46° at 761.1 mm. (4)			
128.7–128.8° at 764 mm. (5)			
128.66° at 760 mm. (6)			n_D^{24} = 1.4402 (10)
128.60° at 760 mm. (7)			
128.6° at 760 mm. (8)		D_4^{20} = 1.2022 (13)	n_D^{20} = 1.44212 (22)
128.1–128.2° at 752 mm. (9)		1.20190 (8)	1.4421 (23)
128.05° at 744 mm. (6)		1.20027 (6)	1.44208 (13)
128.0° at 760 mm. (10)		1.1988 (4)	(9)
128° (11)(12)		1.1981 (22)	1.44197 (6)
127.9–128.1° at 761 mm. (13)			1.44189 (24)
127.9–128.1° at 741 mm. (14)			1.44163 (25)
127.6–128.6° (15)			
127.1–128.1° cor. (16)		D_4^{15} = 1.20720 (13)	n_D^{15} = 1.44382 (22)
127–127.5° (17)			1.44380 (8)
126.5–126.7° at 729 mm. (18)			
51-52° at 22 mm. (1)			
44° at 20 mm. (19)			
43° at 3–4 mm. (20)			

Colorless liq. — miscible with aq. (see also below) and most org. solv.

MISCELLANEOUS PHYSICAL PROPERTIES

Binary Systems Containing $\bar{C}$

$\bar{C}$ + water. For values of D_4^{20} and n_D^{20} (also n_C^{20}, n_F^{20}, n_G^{20}) over whole range 0–100% $\bar{C}$ see (6) cf (22) (23); for thermal anal. of systems see (26). — For study of salting-out of $\bar{C}$ from its aq. solns. (11) or its isolation by ether extraction of aq. solns. satd. with NaCl or Na_2CO_3 (27) see indic. refs. — For concn. of $\bar{C}$, i.e., dehydration of its aq. solns. by distn. of the water with C_6H_6 (28), with 1,2-dichloroethane (ethylene dichloride) (3:5130) (29), or with cyclohexanol (1:6415) (30) see indic. refs. — See also below under azeotropes.

Note that boilg. aq. solns. of $\bar{C}$ undergo slow decompn., e g , about 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11) (presumably by loss of HCl and evoln. of ethylene oxide (1:6105), b.p. 10.7°, and/or (38) acetaldehyde (1:0100), b.p. 20.2°.

$\bar{C}$ with hydrocarbons. *$\bar{C}$ with C_6H_6 (1:7400):* for b.p., vapor-liq. equil., and n_D^{25} see (10). — *$\bar{C}$ with toluene (1:7405):* for b.p., vapor-liq. equil., and n_D^{25} see (10) (see also below under azeotropes).

$\bar{C}$ with alcohols. *$\bar{C}$ with butanol-1 (1:6180):* for b.p, vapor-liq. equil., and n_D^{25} see (10). — *$\bar{C}$ with isobutyl alc. (1:6165):* for b.p , vapor-liq. equil., and n_D^{25} see (10).

$\bar{C}$ with ethers. *$\bar{C}$ with di-isopropyl ether (1:6125):* for b.p., vapor-liq. equil., and

3:5550 1,3-DICHLOROBUTENE-2 (2,4-Dichlorobutene-2) $C_4H_6Cl_2$ Beil. S.N. 11

$$CH_3-\underset{Cl}{C}=CH-\underset{Cl}{CH_2}$$

B.P. 127–129° at 756 mm. (1)	D_4^{20} = 1.1591 (1) (3)	n_D^{20} = 1.47239 (1)
127–128.5° at 753 mm. (2)	1.1582 (2)	1.4695 (2)
61–63° at 70 mm. (1)		
56–57° at 55 mm. (3)		n_C^{20} = 1.46988 (1)
53–54° at 55 mm. (2)		1.4694 (3)
53–54° at 50 mm. (1)		

Colorless liq. with characteristic odor (1). — $\bar{C}$ is formed (5–10% (4) (5) (1)) cf. (10) in synthesis of chloroprene (3:7080). — [For use in mfg. of unsatd. cellulose ethers see (6); in mfg. of unsatd. ethers of alcohols and phenols for use as solvents, disinfectants, etc., see (7) (8).]

[For prepn. of $\bar{C}$ readily and in quantity (1) from vinylacetylene by shaking with an excess (4 moles) of HCl contg. CuCl see (1): from methyl vinyl ketone in 33% yield (together with other products) with PCl_5 at −10° see (2), from 2-chlorobutene-2 (3:7105) (together with other products) by actn. of Cl_2 at 350° see (9); for formn. of $\bar{C}$ (together with other products) from trimethylethylene + Cl_2 see (11).]

$\bar{C}$ passed over silica gel or clay at 245–275° loses HCl yielding (4) 17–18% 3-chlorobutadiene-1,3 ("Chloroprene") (3:7080).

$\bar{C}$ on hydrolysis with steam (12), or *aq.* alk. (5) (12), or *aq.* K_2CO_3 (2), aq. Na_2CO_3 (70–80% yield (4)) or $CaCO_3$ (3) gives 3-chlorobuten-2-ol-1 (3:8207) q.v., b.p. 161–162°. — [Note that $\bar{C}$ with alc. alk. does not hydrolyze or lose HCl but instead gives the corresp. ethers (see details under 3-chlorobuten-2-ol-1 (3:8207)).]

$\bar{C}$ with Cl_2 yields (13) (14) (15) a mixt. of 2,3,4-trichlorobutene-1 (3:9064), 1,2,3,3-tetrachlorobutane (3:9080), and 1,2,2,3,4-pentachlorobutane (3:9070).

35550 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* **54**, 4066–4070 (1932). (2) Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 977–980 (1940); *C.A.* **35**, 2469 (1941). (3) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 658–662 (1937); *Cent.* **1937**, II 371; *C.A.* **31**, 5754 (1937). (4) Klebanskiĭ, [illegible] (1936). [illegible] 6; *Cent* [illegible] 383–408 [illegible] (1935). (7) Berchet (to du Pont), U.S. 2,079,758, May 11, 1937; *Cent.* **1937**, II 2597; *C.A.* **31**, 4676 (1937). (8) Deichsel (to I.G.). Brit. 443,113, Feb. 20, 1936; *Cent* **1937**, I 383–384; *C.A.* **30**, 4873 (1936). (9) N. V. de Bataafsche Petroleum Maatschappij, Brit. 468,016, June 28, 1937; French 810,112, Mar. 15, 1937; *Cent.* **1937**, II 4102; *C.A.* **31**, 8543 (1937). (10) du Pont Co., Brit. 395,131, Aug. 3, 1933; *Cent.* **1933**, 2455: Brit. 387,325; *Cent.* **1933**, I 4525: French 721,532, Mar. 4, 1932; *Cent.* **1932**, II 2107.

[illegible] *Cent.* **1939**, I 4223; *C.A.* **33**, [illegible] 940; *C.A.* **34**, 4392 (1940). (14) Coffman (to du Pont), [illegible] (15) Carothers, Berchet [illegible] 8, 5716 (1934).

3:5552 2-CHLOROETHANOL-1 $CH_2—CH_2OH$ (with Cl on the first CH_2) C_2H_5OCl Beil. I - 337
(Ethylene chlorohydrin, I_1-(170)
β-chloroethanol, I_2-(333)
β-chloroethyl alcohol,
" glycol chlorohydrin ")

B.P.			F.P.		
[132°	at 761 mm.	(1)]	−67.5° (7)	D_4^{25} = 1.1972 (14)	n_D^{25} = 1.44123 (22)
[132.0°		(2)]	(8)	1.19654 (8)	1.4412 (18)
[130-131°	at 760 mm.	(3)]	−69.0°	1.1961 (10)	1.44012 (9)
			(21)	1.1947 (9)	
129.46°	at 761.1 mm.	(4)			
128.7-128.8°	at 764 mm.	(5)			
128.66°	at 760 mm.	(6)			n_D^{24} = 1.4402 (10)
128.60°	at 760 mm.	(7)			
128.6°	at 760 mm.	(8)		D_4^{20} = 1.2022 (13)	n_D^{20} = 1.44212 (22)
128.1-128.2°	at 752 mm.	(9)		1.20190 (8)	1.4421 (23)
128.05°	at 744 mm.	(6)		1.20027 (6)	1.44208 (13)
128.0°	at 760 mm.	(10)		1.1988 (4)	(9)
128°		(11)(12)		1.1981 (22)	1.44197 (6)
127.9-128.1°	at 761 mm.	(13)			1.44189 (24)
127.9-128.1°	at 741 mm.	(14)			1.44163 (25)
127.6-128.6°		(15)			
127.1-128.1° cor.		(16)		D_4^{15} = 1.20720 (13)	n_D^{15} = 1.44382 (22)
127-127.5°		(17)			1.44380 (8)
126.5-126.7°	at 729 mm.	(18)			
51-52°	at 22 mm.	(1)			
44°	at 20 mm.	(19)			
43°	at 3-4 mm.	(20)			

Colorless liq. — miscible with aq. (see also below) and most org. solv.

MISCELLANEOUS PHYSICAL PROPERTIES

Binary Systems Containing C̄

C̄ + water. For values of D_4^{20} and n_D^{20} (also n_C^{20}, n_F^{20}, n_G^{20}) over whole range 0–100% C̄ see (6) cf (22) (23); for thermal anal. of systems see (26). — For study of salting-out of C̄ from its aq. solns. (11) or its isolation by ether extraction of aq. solns. satd. with NaCl or Na_2CO_3 (27) see indic. refs. — For concn. of C̄, i.e., dehydration of its aq. solns. by distn. of the water with C_6H_6 (28), with 1,2-dichloroethane (ethylene dichloride) (3:5130) (29), or with cyclohexanol (1:6415) (30) see indic. refs. — See also below under azeotropes.

Note that boilg. aq. solns. of C̄ undergo slow decompn., e.g., about 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf (11) (presumably by loss of HCl and evoln. of ethylene oxide (1:6105), b.p. 10.7°, and/or (38) acetaldehyde (1:0100), b.p. 20.2°.

C̄ with hydrocarbons. *C̄ with C_6H_6 (1:7400):* for b.p., vapor-liq. equil., and n_D^{25} see (10). — *C̄ with toluene (1:7405):* for b.p., vapor-liq. equil., and n_D^{25} see (10) (see also below under azeotropes).

C̄ with alcohols. *C̄ with butanol-1 (1:6180):* for b.p., vapor-liq. equil., and n_D^{25} see (10). — *C̄ with isobutyl alc. (1:6165):* for b.p., vapor-liq. equil., and n_D^{25} see (10).

C̄ with ethers. *C̄ with di-isopropyl ether (1:6125):* for b.p., vapor-liq. equil., and

n_D^{25} see (10). — *C̄ with di-n-butyl ether (1:7950):* for b.p., vapor-liq. equil., and n_D^{25} see (10). — *C̄ with β,β'-dichloro-diethyl ether (3:6025):* for b.p., vapor-liq. equil., and n_D^{25} see (10) (see below under azeotropes).

C̄ with chlorinated hydrocarbons. *C̄ with 1,2-dichloroethane (ethylene dichloride (3:5130):* for b.p., vapor-liq. equil., and *D* see (31) (see also below under azeotropes). (For use of ethylene dichloride in dehydration of C̄ see (30).)

Azeotropes Containing C̄

Binary azeotropes. C̄ with *water* forms a const.-boilg. mixt., b.p. 97.85° at 760 mm. (26) (8), 97.8° at 760 mm. (23) (32), contg. 45.8 wt. % (8), 43.5 wt. % = 14.7 mole % (32) C̄: constants for this azeotropic mixt. at other press. include the following: at 771 mm., b.p. 96–96.2° (26); at 735 mm., b.p. = 95 8° (33) (11), contg. 42.5 wt. % C̄ (33) (11); at 504 mm., b.p. = 86.4° (23); at 400 mm., b.p. = 80.55°, contg. 40.5 wt. % C̄ (23). — Note that compn. changes only slightly (23) with press. — For study of influence of NaCl (11) (23) or of HCl (11) see indic. refs.

C̄ with *toluene (1:7405)* gives a const.-boilg. mixt., b.p. 106.9°, contg. 27 mole % C̄ (10). — C̄ with *di-n-butyl ether* (1:7950) gives a const.-boilg. mixt., b.p. 123.0°, contg. 68 mole % C̄ (10). — C̄ with *β,β'-dichlorodiethyl* ether (3:6025) gives a const.-boilg. mixt., b.p. 128.2°, contg. 91.8 mole % C̄ (10).

Ternary azeotropes: C̄ with aq. + C_6H_6 (1:7400) gives a const.-boilg. mixt., b.p. 67.0–67.3° (29). — C̄ with aq. + ethylene dichloride (3:5130) gives a const.-boilg. mixt., b.p. 69.6° (29). — C̄ with aq. + 1,1,2-trichloroethylene (3:5170) gives a const.-boilg. mixt., b.p. 70.8–71.5° (29).

Miscellaneous Physical Properties of C̄

[For sepn. of C̄ from gas mixts. by adsorption (?) on $Mg(ClO_4)_2$ or other perchlorates see (34).]

USES OF C̄

The manifold uses of C̄, based upon both its physical and its chemical characteristics, cannot here be reviewed in detail; however, some examples include the following.

[For use in sepn. of butadiene from hydrocarbon mixts. (35), in dewaxing and removing naphthenes from mineral lubricating oils (36), in refining of rosin (37), in extraction of pine lignin (38) (39), as solv. for various resins (40), as solv. for cellulose acetate (41) or cellulose ethers (42), for addn. to rayon spinning baths (43) see indic. refs.]

PHYSIOLOGICAL AND BIOCHEM. BEHAVIOR OF C̄

[For study of pharmacol. of C̄ (or its phosphoric esters, etc.) see (44); for reports of poisoning by C̄ see (45) (46); for study of toxicity of vapor of C̄ see (403).]

[For effect of C̄ upon amylase (47) (48) or lipase (49) see indic. refs.; for use of C̄ in prod. of yeast of depressed enzymatic activity see (50).]

DETERMINATION OF C̄

[For colorimetric detn. of C̄ by reactn. with diazotized sulfanilic acid in alk. soln. at 25° see (106) (note that method involves oxidn. of C̄ by the reagt. to chloroacetaldehyde (3:7212) and color formn. with latter); for detn. of C̄ in aq. solns. by refractometry see (11) (25) (6) (23).]

PREPARATION OF $\bar{C}$

From ethylene. *With hypochlorous acid, e.g., from Cl_2 + aq.* — $\bar{C}$ is usually prepd. from ethylene by addn of HOCl; the HOCl may be obtained by use of Cl_2 + aq. (sometimes in the pres. of alk. acceptors for the simultaneously formed HCl), by use of organic hypochlorites, or other org. cpds which hydrolyze to give HOCl.

[For scientific papers discussing prepn. of $\bar{C}$ from ethylene + HOCl (Cl_2 + aq.) see (401) (11) (51) (52) (53) (54) (55) (56) (57) (58) (59); for very old work see (60); for examples of patents employing this method see citations (61)-(82) cf. (402), inclusive; for study of metal-corrosion problems involved in this method of prepn. of $\bar{C}$ see (83).]

With organic hypochlorites (e.g., ter-butyl hypochlorite (3:7165)). [For patents on prepn. of $\bar{C}$ from ethylene + *ter*-butyl hypochlorite see (84) (85).]

With N-chlorourea. [For prepn. of $\bar{C}$ from ethylene with *N*-chlorourea in 5% H_2SO_4 contg. $CuCl_2$ at 0° (yield: 60-70% $\bar{C}$ accompanied by 2% ethylene dichloride (3:5130)) see (86).]

From ethylene glycol (1:6465). [For prepn. of $\bar{C}$ from ethylene glycol satd. with HCl gas and htd. in s.t. (12) (90), or treated at 160° (87) (4) or 180° (88) with stream of HCl (yields: 70-80% (88), 60% (87)), see indic. refs.; note that ethylene glycol with excess conc. HCl in s.t. at 100° gives no $\bar{C}$ (89) but only ethylene dichloride (3:5130), while mere distn. with conc. HCl (9 moles) gives (15) only 12% $\bar{C}$.)]

[For prepn. of $\bar{C}$ from ethylene glycol with S_2Cl_2 (2.5 wt. pts. (91)) on refluxing (yields: 82.5% (92), 72.8% (91)) (93) (94) (95) see indic. refs.: for formn. of $\bar{C}$ from glycol with $SiCl_4$ see (96).]

From ethylene glycol esters. [For patents on prepn. of $\bar{C}$ from ethylene glycol diformate (1:3402) with HCl gas at 100° via formn. of β-chloroethyl formate and subsequent alcoholysis of latter with MeOH/HCl (97), or from ethylene glycol diacetate (1:3511) with EtOH + HCl at 125-135° under press. (EtOAc is also formed) (98), see indic. refs.]

From ethylene oxide (1:6105). [For formn. of $\bar{C}$ from ethylene oxide with liq. HCl (99) or with S_2Cl_2 (100) (other prods. are also formed) see indic. refs.]

From other miscellaneous sources. [For formn. of $\bar{C}$ from 1,2-dichloroethane (ethylene dichloride) (3:5130) by conversion with SO_3 below 45° to β-chloroethyl chlorosulfonate (see below) and subsequent hydrolysis to $\bar{C}$ (101); from *bis*-(β-chloroethyl) sulfate (see below) by refluxing with aq (102); from β-chloroethyl trichloroacetate (3.6410) by shaking with aq. (103); from β-chloroethyl vinyl ether (3:7464) on distn. with aq. + trace of HCl (acetaldehyde is also formed) (104); from chloroacetaldehyde (3:7212) by reduction of carbonyl group with EtOMgBr (105) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis of $\bar{C}$. [$\bar{C}$ in s.t. at 184° for 10 hrs yields (107) 1,2-dichloroethane (ethylene dichloride) (3:5130) and acetaldehyde (1:0100) (the latter partially as aldehyde resin); for study of rate of decompn. of $\bar{C}$ at 368° see (108).]

Behavior with Inorganic Reactants

Reduction of $\bar{C}$. [$\bar{C}$ with Na/Hg + aq. (109), or $\bar{C}$ in aq. soln. in pres. of alk. with H_2 at atm. press. + cat. (110), yields ethyl alcohol (1:6130); in latter method reduction is facilitated by NaOH, less so by $Ca(OH)_2$ or $CaCO_3$; using Pd/$CaCO_3$ yield of EtOH is 91%; using Ni yield of EtOH is 80% accompanied by 20% ethylene glycol (1:6465) (110).]

Oxidation of $\bar{C}$. $\bar{C}$ on oxidn. with CrO_3 yields (111) chloroacetic acid (3:1370).

Behavior with H_2O. $\bar{C}$ on boilg. with aq. undergoes gradual decomposition: e.g., 10% in 8 hrs. (23), 50% in 5 hrs. (107) cf. (11), presumably by loss of HCl and formation of ethylene oxide (1:6105), acetaldehyde (1:0100) etc. — [Note that $\bar{C}$ with aq. vapor over $ZnCl_2$ + ZnO at 250–255° yields (112) acetaldehyde (1:0100).]

Behavior with inorganic acids. (See also below under behavior with salts of inorganic acids.)

With H_2SO_4 $\bar{C}$ with conc. H_2SO_4 readily dissolves and according to conditions yields either β-chloroethyl hydrogen sulfate or *bis*-(β-chloroethyl) ether. (Note that $\bar{C}$ with SO_2Cl_2 (see below) gives *bis*-(β-chloroethyl) sulfate.)

[For study of rate and extent of formn. of β-chloroethyl HSO_4 with conc. or fumg. H_2SO_4 at 25° see (14); for reactn. of barium salt of this prod. with aniline see (113).]

$\bar{C}$ with conc. H_2SO_4 (17% by wt. of $\bar{C}$) refluxed 6 hrs. gives (114) *bis*-(β-chloroethyl) ether (3:6025).

With HNO_3. [$\bar{C}$ with HNO_3/H_2SO_4 (115) (116) gives (92% yield (115)) β-chloroethyl nitrate, $ClCH_2CH_2ONO_2$, b.p. 149–150°; for use of this prod. in explosives see (115) (117); for use as ignition accelerator in Diesel engine fuels see (118) (119) (120).]

With HNO_2. [$\bar{C}$ with HNO_2 (from $NaNO_2$ + HCl) at −5° gives (70% yield (121)) (122) (123) β-chloroethyl nitrite $ClCH_2CH_2ONO$, b.p. 90–91° (121), 89–89.5° (122), D_-^{20} = 1.212 (122), n_D^{20} = 1.4125 (122). (This prod. is not to be confused with the isomeric chloro-nitro-ethanes Beil. I-101.)]

Behavior with salts of inorganic acids. (For behavior with NaCN, anhyd. Na_2CO_3, NaSCN, etc., see further below under organic reactants; for behavior with NaSH see further below under alkali reactants.)

With alkali iodides. $\bar{C}$ with NaI in hot alc. (124) (125) or boiling acetone (126) for 16 hrs. (127) (better 4 hrs. (20)), or with KI in alc. at room temp. for 24 hrs. (128) gives (95% yield (127)) β-iodoethanol (ethylene glycol iodohydrin), b.p. 176–177° dec. (124), 86–87° at 25 mm. (20), 85–88° at 25 mm. (127), 85° at 25 mm. (124), 61° at 7 mm. (4), D_4^{20} = 2.1968 (4), n_D^{20} = 1.57134 (24). [For study of rate of reaction of $\bar{C}$ with KI in dry acetone at 50° and 60° see (16).]

With alkali sulfides (for alkali sulfhydrates, e.g., NaSH, see below). — [$\bar{C}$ with aq. K_2S (129) or with aq. Na_2S (11) (130) (131) (132) at 30–35° for 1 hr. (33) splits out 2 NaCl giving (yields: 90–95% (11), 79–86% (33)) *bis*-(β-hydroxyethyl) sulfide ("thiodiglycol") [Beil. I-470, I_1-(244), I_2-(525)], b.p. 164–166° at 20 mm (33), 130° at 2 mm. (131), 104° at 0.005 mm. (132), f p. = −16° (132), D_4^{20} = 1.1821 (132), 1.1819 (132), n_D^{20} = 1.52031 (132), misc. with aq., readily sol. alc., acetone, EtOAc, or $CHCl_3$, but spar. sol. ether, C_6H_6, or CCl_4 (131) (corresp. dibenzoate, m.p. 65° (133), di-(p-nitrobenzoate), m.p. 107.7° (134), *bis*-(N-phenylcarbamate), m.p. 128.5–129.5° (131)). — Note that this prod. ("thiodiglycol") with $\bar{C}$ at 100° for 13 hrs. (131) adds to form *tris*-(β-hydroxyethyl)sulfonium chloride $(HOCH_2CH_2)_3SCl$, non-hygroscopic ndls., m.p. 126–127° (132), 125–126° (131). Note also that $\bar{C}$ (1 mole) + Na_2S + 1-chloropropanol-2 (propylene chlorohydrin) (3:7747) yields (135) a mixed deriv., viz., β-hydroxyethyl β-hydroxy-n-propyl sulfide.]

With alkali selenide. [$\bar{C}$ with aq. Na_2Se yields (136) *bis*-(β-hydroxyethyl) selenide.]

With alkali disulfide. [$\bar{C}$ with aq. Na_2S + S gives (46% yield (137)) (138) *bis*-(β-hydroxyethyl) disulfide [Beil. I-471, I_2-(528)], b.p. 155° at 30 mm., D_4^{20} = 1.3375 (137).]

With $NaHSO_3$. [$\bar{C}$ with solid $NaHSO_3$ in s.t. at 170–180° for several hrs. gives (139) the salt of 2-hydroxyethanesulfonic acid-1 ("isethionic acid").]

With Na_3PO_4. [$\bar{C}$ with satd. aq. Na_3PO_4 as directed (140) cf. (3) gives (30% yield (140)) di-sodium β-hydroxyethyl phosphate, cryst. from aq. alc. as hexahydrate, m p. 61° (140).]

With Na_3AsO_3. [$\bar{C}$ with aq. alk. Na_3AsO_3 (from As_2O_3 in aq. alk.) as directed (141) (142) (143) cf. (144) (145) gives β-hydroxyethylarsonic acid (also known as β-hydroxyethylarsinic acid) = $HOCH_2CH_2AsO(OH)_2$, very sol. aq. but forming spar. sol. monohydrated calcium salt (141).]

With Na_2SnO_2. [$\bar{C}$ with aq. alk. Na_2SnO_2 (from $SnCl_2$ + aq. NaOH) gives (146) salt of β-hydroxyethylstannonic acid = $HOCH_2CH_2.SnO(OH)$.]

Behavior with acid halides of inorganic acids. *With thionyl chloride ($SOCl_2$).* [$\bar{C}$ with $SOCl_2$ (small excess) in cold gives (83% yield (147)) β-chloroethylsulfinyl chloride = $ClCH_2CH_2OS(O)Cl$, b.p. 93–95° at 40 mm., 84–85° at 20 mm., D_4^{20} = 1.5010, which upon attempted distn. at ord. press. dec. into SO_2 + ethylene (di)chloride (3:5130) (147). — However, $\bar{C}$ (excess) with $SOCl_2$ at elevated temp. (147) or $\bar{C}$ (1 mole) with $SOCl_2$ (1 mole) in cold (148) gives (75% yield (148)) cf. (156) *bis*- (β-chloroethyl) sulfite = $(ClCH_2CH_2O)_2SO$, b.p. 133° at 12 mm. (148), 117.5–118° at 4 mm. (147), D_0^{20} = 1.422, $n_D^{20.5}$ = 1.481 (148).]

With sulfuryl chloride (SO_2Cl_2) [$\bar{C}$ with SO_2Cl_2 in cold gives (149) (70% yield (122)) β-chloroethyl chlorosulfonate = $ClCH_2CH_2O.SO_2Cl$ [Beil. I_2-(336)], b.p. 101° at 23 mm., $D_-^{20.5}$ = 1.552, $n_D^{18.3}$ = 1.4587 (122). — However, $\bar{C}$ with SO_2Cl_2 under reflux (121) (or β-chloroethyl chlorosulfonate + β-chloroethyl nitrite (above) (122)) gives (50% yield (121)) *bis*-(β-chloroethyl) sulfate = $(ClCH_2CH_2O)_2SO_2$ [Beil. I_2-(336)], b.p. 154–154.5° at 8 mm. (121), 130° at 3.5 mm. (122), m.p. + 11° (121), D_4^{20} = 1.4801 (121), n_D^{20} = 1.4622 (121), 1.4620 (122).]

With phosphoryl chloride ($POCl_3$). [$\bar{C}$ with $POCl_3$ at 0° (150) or in CCl_4 at room temp. (151) gives (46–47% yield (151)) β-chloroethylphosphoryl dichloride = $ClCH_2CH_2OP(O)Cl_2$ [Beil. I_2-(337)], b.p. 108–110° at 15 mm. (151). — $\bar{C}$ with $POCl_3$ in pyridine at −20° gives (140) the salt of mono-(β-chloroethyl)phosphoric acid = $ClCH_2CH_2OP(O)(OH)_2$ [Beil. I_1-(170), I_2-(336)]. — $\bar{C}$ with $POCl_3$ in CCl_4 refluxed 16 hrs. gives (60% yield (152) cf. (140)) tri-(β-chloroethyl) phosphate = $(ClCH_2CH_2O)_3PO$ [Beil. I_2-(337)], b.p. 180–182° at 2–3 mm., D_{20}^{20} = 1.428 (152). — For patent on reaction of $\bar{C}$ with $POCl_3$ see (153).]

With boron trifluoride (BF_3). [$\bar{C}$ with BF_3 forms a molecular compound (154) $BF_3.2\bar{C}$ which can be distilled in vac. without decompn.; b.p. 59° at 2 mm., D_4^{20} = 1.4009, $n_{He}^{17.4}$ = 1.40841 (154).]

With silicon tetrachloride ($SiCl_4$). [$\bar{C}$ (4 moles) with $SiCl_4$ (1 mole) yields (155) (96) tetra-(β-chloroethyl) orthosilicate, $(ClCH_2CH_2O)_4Si$ [Beil. I-337, I_2-(337)], b.p. 195–200° at 15 mm. (156), 170–180° at 8 mm. (96) (also obtd. (156) from $SiCl_4$ + β-chloroethyl nitrite (above)).]

Behavior with alkalies. $\bar{C}$ with alkalies (or appropriate acid acceptors) loses HCl to yield according to conditions either ethylene glycol (1:6465) or ethylene oxide (1:6105).

[E.g., $\bar{C}$ with aq. NaOH on htg. hydrolyzes to ethylene glycol (1:6465), for general articles on this process see (54) (157) (158) (22); for studies of kinetics of the reaction see (404) (18) (159) (160) (161); for examples of patents on hydrolysis of $\bar{C}$ to ethylene glycol by use of aq. alkali or alkaline-earth hydroxides, carbonates, or bicarbonates see (162) (163) (63) (164) (165) (166) (167).]

[$\bar{C}$ added dropwise to 70% aq. NaOH (168) (169) or hot CaO (170) gives ethylene oxide (1:6105), b.p. +10.7°; for patents on this conversion see (171) (172) (173) (174) (175).]

Behavior with alkali sulfhydrate. [$\bar{C}$ with NaSH (from $Na_2S.9H_2O$ satd. with H_2S (137)) at 55–65° (137) (176) or $\bar{C}$ with NaSH in alc. for 36 hrs. at room temp. (177) gives (yields: 55% (176), 50–55% (137), 26–30% (177)) β-hydroxyethyl mercaptan ("monothioethylene glycol") = $HOCH_2CH_2SH$ [Beil. I-470, I_2-(523)], b.p. 157–158° dec. at 742

mm. (178), 61° at 18 mm. (179), 58° at 18 mm. (137), 55° at 13 mm. (178), 52° at 12 mm. (177); D_4^{20} = 1.1143 (178); n_D^{20} = 1.4996 (178) (corresp. *bis*-(*N*-phenyl)carbamate, m.p. 146° (178); corresp. metallic mercaptide derivs. many of which have m.p.'s (178)).]

Behavior with ammonia (*for amines see below under behavior with organic reactants*). [$\bar{C}$ with aq. NH_4OH gives (180) a mixt. of three hydroxyamines, viz., β-hydroxyethylamine (2-aminoethanol-1) [Beil. IV-274, IV_1-(424), IV_2-(717)]; *bis*-(β-hydroxyethyl)amine ("diethanolamine") [Beil. IV-283, IV_2-(729)]; and *tris*-(β-hydroxyethyl)amine ("triethanolamine") [Beil. IV-285, IV_2-(729)]. — Although all three of these products are now extremely important industrial compounds, they are usually manufactured from ethylene oxide with NH_3 and details lie beyond the scope of this text. — However, for a useful monograph see (181).]

Behavior with hydrazine ($NH_2.NH_2$). [$\bar{C}$ with 1 mole hydrazine loses HCl yielding (182) β-hydroxyethylhydrazine + hydrazine hydrochloride; $\bar{C}$ with 2–3 moles hydrazine yields (182) ethylene oxide accompanied by a little *N,N-bis*-(β-hydroxyethyl)hydrazine.]

BEHAVIOR OF $\bar{C}$ WITH ORGANIC REACTANTS

Behavior with hydrocarbons. [$\bar{C}$ with C_6H_6 + $AlCl_3$ (followed by aq.) is claimed (183) to yield β-phenylethyl alc. (1:6505), but this has subsequently been denied (184) where 1,2-diphenylethane (bibenzyl) (1:7149) and resin were the only prods. obtd. (See also below under behavior of $\bar{C}$ with organometallic cpds.)]

Behavior with organic hydroxyl compounds. *With alcohols* (see also below under carbohydrates). $\bar{C}$ (anhydrous) with sodium alkoxides (from prim. or sec. aliphatic or arom. alcs. + Na) on htg. splits out NaCl giving the corresp. mono ethers of ethylene glycol.

[E.g., $\bar{C}$ with NaOMe gives (35% yield (185)) β-hydroxyethyl methyl ether (1:6405) q.v.; $\bar{C}$ with NaOEt gives (60% yield (185)) β-hydroxyethyl ethyl ether (1:6410) q.v.; $\bar{C}$ with NaOPr gives (40% yield (185)) β-hydroxyethyl *n*-propyl ether (1:6414) q.v.; $\bar{C}$ with NaOisoPr gives (25% yield (185)) β-hydroxyethyl isopropyl ether (1:6413) q.v.; $\bar{C}$ with NaOBu gives (30% yield (185)) β-hydroxyethyl *n*-butyl ether (1:6430) q.v.; $\bar{C}$ with NaOiso-Bu gives (36% yield (185)) β-hydroxyethyl isobutyl ether (1:6235-A); $\bar{C}$ with NaOAm gives (30% yield (185)) β-hydroxyethyl *n*-amyl ether, b.p. 181° at 745 mm. (185).]

[$\bar{C}$ with $NaOCH_2C_6H_5$ similarly gives (186) (187) ethylene glycol monobenzyl ether (1:6533) q.v.]

With carbohydrates (or their relatives). [$\bar{C}$ with *d*-glucose + HCl yields (188) cf. (189) 2-chloroethyl-*d*-glucoside.]

[$\bar{C}$ with "acetobromglucose" + Ag_2CO_3 (190) (193) in C_6H_6 (189) (191) gives (yields: *69% (189), 45–50% (190)) tetra-acetyl-β-d-(β-chloroethyl)glucoside (tetra-acetyl-β-d-*glucosido-ethylene chlorohydrin), m.p. 119–120° (192), 118.5–119.5° (189), 114° cor. (190) (191). — For isomerization of this prod. (in boilg. $CHCl_3$ for 6½ hrs.) to tetra-acetyl-α-*d*-(β-chloroethyl)glucoside, m.p. 82–83°, see (194).]

[$\bar{C}$ with "acetobromogalactose" + Ag_2CO_3 (190) (194) in C_6H_6 (191) gives (77% yield (194)) tetra-acetyl-β-*d*-(β-chloroethyl)galactoside, m.p. 117° cor. (190) (191), 115.5–116.5° (194).]

[For analogous prepn. from $\bar{C}$ of triacetyl-β-*d*-(β-chloroethyl)xyloside, m.p. 137° cor., or of hepta-acetyl-β-*d*-(β-chloroethyl)lactoside, m.p. 78–80°, see (190) (191).]

[For condens. of $\bar{C}$ with mannitol (1:5830) or sorbitol (1:5820) see (195).]

[For use of $\bar{C}$ in degradation ("depolymerization") of cellulose or starch see (196) (197); for use of $\bar{C}$ + NaOH in introduction of β-hydroxyethyl groups into cellulose see (198).]

With aliphatic mercaptans. $\bar{C}$ with salts of alkyl or alkaryl mercaptans gives the corresp. S-monoethers of monothioethylene glycol.

[E g., $\bar{C}$ with NaSMe in abs. alc. (199) (200) or ether (201) (202) or less advantageously

$\bar{C}$ with KSMe in aq. alc. (201) gives (yields 74–82% (199), 78% (201), 40% (199)) β-hydroxyethyl methyl sulfide (β-methylmercaptoethanol) [Beil. I_2-(524)], b.p. 80.5–81° at 30 mm. (201), 68–70° [illegible] with MeI in dry ether [illegible] iodide, hygroscop. cryst. from MeOH/ether, m.p. 60–62° (202). — $\bar{C}$ with EtSH in alc./NaOEt (203), in alc. KOH (132), or even in conc. aq. KOH (204) gives (yield 70–74% (203)) β-hydroxyethyl ethyl sulfide [Beil. I-470, I_2-(525)], b.p. 184° (204) (132), 182–184° u.c. (203), $D_4^{20} = 1.0166$ (132), $n_D^{20} = 1.48669$ (132).]

[$\bar{C}$ with n-BuSH in hot aq. NaOH refluxed 1 hr. gives (81% yield (205)) β-hydroxyethyl n-butyl sulfide [Beil. I_2-(525)], b.p. 92–93° at 3 mm., $D_{25}^{25} = 0.9693$, $n_D^{20} = 1.4800$ (205). — $\bar{C}$ with allyl mercaptan in conc. aq. KOH gives (50% yield (206)) β-hydroxyethyl allyl sulfide [Beil. I_2-(525)], b.p. 91° at 12 mm., $D_{20}^{20} = 1{,}0283$ (206). — $\bar{C}$ with $NaSCH_2C_6H_5$ in aq. soln. gives (100% yield (179)) β-hydroxyethyl benzyl sulfide, b.p. 169° at 18 mm.]

[$\bar{C}$ with ethylene dithioglycol ($HSCH_2CH_2SH$) + powdered NaOH htd. 1 hr. gives (177) ethylene dithioglycol *bis*-(β-hydroxyethyl ether) = $HOCH_2CH_2—S—CH_2CH_2—S—CH_2CH_2OH$ [Beil. I_2-(533)], lfts., m.p. 62–63°.]

With phenols. [$\bar{C}$ with phenol (1:1420) in aq. NaOH (207) or alc. NaOEt (208), or $\bar{C}$ with $NaOC_6H_5$ on htg. (17) (209), or $\bar{C}$ with KOC_6H_5 at 150° for 6 hrs. (210), or $\bar{C}$ with phenol salt refluxed 8 hrs. (211) gives (yields: 84% (17), 79% (207), 55–62% (211), 50% (209)) β-hydroxyethyl phenyl ether (β-phenoxyethanol) (1:6518) q.v., b.p. at 80 mm. = 165° (211), 163–166° (208), 163–167° (210), b.p. 128–130° at 20 mm. (17), 134–135° at 18 mm. (209). — (Note that $\bar{C}$ with $NaOC_6H_5$ in pres. of Et_3N gave only 12.5% yield (212) of β-phenoxyethanol.)]

[Similarly $\bar{C}$ with aq. sodium o-nitrophenolate in s.t. at 125° for 20 hrs. gives (213) β-(o-nitrophenoxy)ethanol, oil, b.p. 180–182° at 4 mm., m.p. 35–36° (215) (corresp. acetate, oil; corresp. benzoate, m.p. 75–76° (213)); $\bar{C}$ with m-nitrophenol with 40% aq. KOH at 100° for 2 hrs. (213), or with 2 *N* NaOH refluxed 4 hrs. (214), gives β-(m-nitrophenoxy)-ethanol, m.p. 90–91° (213), 88° (214), 87–88° (215); $\bar{C}$ with sodium p-nitrophenolate in 50% alc. in s.t. at 120° for 23 hrs. (213), or in boilg. AmOH (216) (217), gives β-(p-nitrophenoxy)ethanol, m.p. 101–102° (213), 94–95° (216), 92–94° (215) (corresp. acetate, m.p. 85–87°, corresp. benzoate, m.p. 116° (213).]

[Analogous condensations of $\bar{C}$ with other monohydric phenols include the following: for $\bar{C}$ with o-cresol (1:1400) (218), with β-naphthol (1:1540) (218), with m-methoxyphenol (1:1765) (219) (220) (221), with methyl p-hydroxybenzoate (1:1549) (222), with p-bromophenol (218), with p-acetylaminophenol (213), with m-diethylaminophenol (212), with 8-hydroxyquinoline (212) see indic. refs.]

[Analogous condensations of $\bar{C}$ with polyhydric phenols include the following: with pyrocatechol (1:1520) (223), resorcinol (1:1530) (224) (218), 4-acetylresorcinol (219), 4-ethylresorcinol (219) see indic. refs.]

With thiophenols. [$\bar{C}$ with thiophenol in alc. NaOEt (225) (203) or in 10% aq. KOH (226) gives (76% yield (203)) β-hydroxyethyl phenyl sulfide, b.p. 245° (203), 144.5° at 26 mm. (203), 134–135° at 7 mm. (225), 115–116° at 2 mm. (226), $D_4^{20} = 1.1431$ (226), $n_D^{25} = 1.5897$ (225), $n_D^{20} = 1.5917$ (226). — $\bar{C}$ with p-toly mercaptan in conc. aq. NaOH at 100° for 2 hrs gives (83% yield (133)) (227) β-hydroxyethyl p-tolyl sulfide, b.p. 282–283° dec., 174° at 30 mm. (133).]

[For analogous condens. of $\bar{C}$ with o-nitrophenyl mercaptan (228), m-nitrophenyl mercaptan (228), p-nitrophenylmercaptan (228) (229), o-carboxythiophenol (230), and many other thiophenols (231) see indic. refs.]

Behavior of $\bar{C}$ with organic ethers (or epoxy cpds.). [$\bar{C}$ with ethylene oxide (1:6105) + conc. H_2SO_4 gives (30–35% yield (232)) 2-(β-chloroethoxy)ethanol-1 (3:9185) accompanied

by other prods.: for behavior of Č with epichlorohydrin (3:5358) or with α-ethyl-α-methylethylene oxide see (232). — Č with α,β′-dichlorodiethyl ether (3:9150) stood 24 hrs. at room temp., then htd. 1 hr., gives (27% yield (233)) acetaldehyde *bis*-(β-chloroethyl) acetal. (see below). — Č with *bis*-(α-chloroethyl) sulfide gives (234) β-trithioacetaldehyde, m.p. 125°. — For behavior of Č with 2,3-dichlorodioxane (3:9105) see (235); with 1,4-dithiane see (131).]

Behavior of Č with carbonyl compounds. *Č with aldehydes or their polymers.* [Č with paraformaldehyde (1:0080) + dry HCl gas gives (yields: 65% (237), 55% (236)) (238) (239) chloromethyl β-chloroethyl ether [Beil. I-581, I_2-(645)], b.p. 145–147° (237), 46° at 10 mm. (236); D_4^{20} = 1.2817 (237), 1.2814 (236); n_D^{20} = 1.4578 (236), 1.4592 (237). — Note that this prod. with Č (239), or Č (8 wt. pts.) + paraformaldehyde (1 wt. pt.) + $CaCl_2$ + HCl gas refluxed 5 min. (38) gives formaldehyde *bis*-(β-chloroethyl)acetal [Beil. I-575], b.p. 218–219° (239), 218.1° at 760 mm. (240), b.p. 93–94° at 11 mm. (38), now an industrial prod. in U.S. because of its use in manufact. of self-sealing gasoline tanks (240).]

[Č with acetaldehyde (1:0100) (241) (20) (233) or paraldehyde (1:0170) (236) + HCl gas gives according to circumstances either α-chloroethyl β-chloroethyl ether (3:9150) q.v. or acetaldehyde *bis*-(β-chloroethyl)acetal, b.p. 194–196° dec. (233), 109–110° at 30 mm. (20), 106° at 17 mm., D_{-}^{19} = 1.1712, $n_D^{18.2}$ = 1.4532 (233).]

[Č with propionaldehyde (1:0110) + HCl gas gives (51% yield (236)) β-chloroethyl α-chloro-*n*-propyl ether, b.p. 60° at 10 mm., D_4^{20} = 1.1399, n_D^{20} = 1.4496 (236).]

[Č with *n*-butyraldehyde (1:0130) + HCl gas gives (70% yield (236)) β-chloroethyl α-chloro-*n*-butyl ether, b.p. 71° at 10 mm., D_4^{20} = 1.1009, n_D^{20} = 1.4471 (236).]

Č with diketene. [Č with diketene (242) gives (243) β-chloroethyl acetoacetate.]

Behavior of Č with organic acids. Č with organic acids under appropriate conditions behaves conventionally as a substituted ethyl alcohol yielding the corresponding β-chloroethyl esters. Since the number of possibilities is enormous, no attempt can be made here to list all such cases; only a few typical examples must suffice. Note, moreover, that, because during ordinary esterification hydrolysis of the chlorine atom of Č may occur, many esters of Č are best made from its reaction with acyl halides q.v.

[Č with anhydrous formic acid (1:1005) in pres. of anhydr. Na_2SO_4 (244) or of HCl gas (245) gives β-chloroethyl formate, b.p. 132° at 764 mm. (245), 127–129° at 768 mm. (244), D_4^{20} = 1.2214 (244); for study of rate of esterification of Č by formic acid under various circumstances see (246).]

[Č with anhydr. oxalic acid (1:0535 on satn. with HCl gas and htg. at 100° gives (245) di-(β-chloroethyl) oxalate (3:0572), m.p. 45°.]

[Č with 2-hydroxy-5-methylbenzoic acid (*p*-cresotinic acid) + conc. H_2SO_4 gives β-chloroethyl *p*-cresotinate, b.p. 136–139° at 10 mm. (247).]

[Č with *p*-aminobenzoic acid + conc. H_2SO_4 gives (248) (249) β-chloroethyl *p*-aminobenzoate.]

Behavior of Č with salts of organic acids. Č with sodium salts of organic acids on htg. eliminates NaCl yielding the corresp. β-hydroxyethyl esters; however, not infrequently secondary reactions of this product then occur or can readily be caused to occur, such as loss of water, ring closure, etc.

[Č with aq. NaCN at 45–50° for 5 hrs. (250) (251), or with alc. NaCN at 100° for 6 hrs. (88) (27), or with KCN in 50% alc. (252) or boilg. alc. (253) (254), gives (yields: 86% (27), 85–95% (251), 79–80% (250), 71% (253)) β-hydroxyethyl cyanide (β-hydroxypropionitrile = hydracrylonitrile = ethylene cyanohydrin) [Beil. III-298, III_1-(113), III_2-(213)], b.p. 116–118° at 20 mm. (250), 110° at 15 mm. (27) (253), 107–109° at 12 mm. (250).]

[Č (1 mole) with $NaHCO_3$ (1 mole solid) or with Na_2CO_3 (½ mole solid) as directed (255) is claimed to give (80% yield) monomeric ethylene glycol carbonate $(CH_2)_2O_2CO$.]

[C̄ (1 mole) with KSCN (1 mole) in excess C̄ (1.5 moles as solv.) on warming does *not* yield the expected β-hydroxyethyl thiocyanate, since this prod. spontaneously undergoes bimolecular self-condensation evolving COS and producing (45% yield (256)) 1-(β-hydroxyethyl)imidazolidthione-2, m.p. 167–168° dec.; for behavior of this prod. with ethereal HCl see (257).]

[C̄ with NaOBz at 145° (258) or C̄ with NaOBz + a little Et_2NH at 130° for 4 hrs. (259), or C̄ with KOBz as directed (260), gives (yields: 85% (259), 33% (260)) ethylene glycol monobenzoate (β-hydroxyethyl benzoate), m.p. 36.5–37.5° (261), 36–37° (260) cf. (259); b.p. 173° at 21 mm. (259), 156° at 14 mm. (260), 150–151° at 10 mm. (261) (corresp. p-toluenesulfonate, m.p. 74–75° (262)).]

[C̄ with Na p-nitrobenzoate + a little Et_2NH at 130° for 4 hrs. (259), or C̄ with K p-nitrobenzoate in C_6H_6 in s t. at 100° (263), gives (yields: 83% (259), 60% (263)) ethylene [illegible]

[illegible] indic. refs.]

Behavior of C̄ with acid chlorides of organic acids. C̄ with acid chlorides of organic acids behaves as a substituted primary alcohol splitting out H from its OH with Cl from the acid chloride to yield the corresp. β-chloroethyl esters. No attempt can be made here to list all possible cases, but the following text will furnish ample illustrative examples.

With acid chlorides of aliphatic acids. [C̄ with acetyl chloride (3:7065) gives (yields: 90% (267), 82% (248)) (268) β-chloroethyl acetate (3:5735) q.v. — C̄ with trichloroacetyl chloride (3:5420) + pyridine in ether gives (45% yield (103)) (275) β-chloroethyl trichloroacetate (3:6510) q.v. — C̄ with sorbyl chloride ($CH_3CH=CH—CH=CH—CO.Cl$) [Beil. I-484, I_1-(453)] gives alm. quant (269) β-chloroethyl sorbate, b.p. 115° at 15 mm. (269). — For studies of rate of reactn. of C̄ with various acyl chlorides in dioxane soln. at 15°, 25°, and 35° see (270). — C̄ with malonyl (di)chloride (3:9030) gives *bis*-(β-chloroethyl) malonate, b p. 164° at 15 mm. (271).]

With various chloroformates. C̄ with carbonyl chloride (phosgene) (3:5000) at room [illegible] β-chloroethyl chloro- [illegible] below) is formed.]

[illegible] gives (61% yield (274)) β-chloroethyl trichloromethyl carbonate = $ClCH_2CH_2O.CO.O.CCl_3$, b.p. 115° at 16 mm., 110° at 12 mm., $D_4^{20} = 1.5664$, $n_D^{20} = 1.4748$ (274).]

[C̄ *with β-chloroethyl chloroformate (3:5780)* gives *(70% yield (121))* di-(β-chloroethyl) carbonate (3:6790) q.v.]

With acid chlorides of aromatic acids. [C̄ with benzoyl chloride on htg. gives (yields: *90% (276), 84.5% (277), 55% (263))* β-*chloroethyl* benzoate (3:8860) q.v.]

Behavior of C̄ with organic esters of inorganic acids. [C̄ with Me_2SO_4 at 120° as directed gives (60% yield (126)) β-chloroethyl methyl ether (β-methoxyethyl chloride) (3:7265) q.v.]

[C̄ with Et_2SO_4 + solid NaOH on htg. gives (278) ethylene glycol monoethyl ether ("Cellosolve") (1:6410); note, however, that C̄ with EtOH + conc. H_2SO_4 at 145° gives (279) β-chloroethyl ethyl ether (3:7463).]

[C̄ (1 mole) with ethyl metaphosphate (1 mole) stood 4 days at room temp. (280) cf. (281) gives β-chloroethyl ethyl hydrogen phosphate (isolated as barium salt); however, C̄ + ethyl metaphosphate in $CHCl_3$ refluxed 3 hrs. gives (140) β-chloroethyl dihydrogen phosphate (isolated as barium salt).]

C̄ with organic hypochlorites (or mixtures which yield them) gives ethers [e.g., C̄ with *ter*-butyl hypochlorite (3:7165) + ethylene gives (60.8% yield (282)) β,β′-dichlorodiethyl

ether (3:6025). — $\bar{C}$ with *N,N*-dichlorobenzenesulfonamide + butene-1 in $CHCl_3$ at −15° gives (283) (probably via formn. and addn. of β-chloroethyl hypochlorite) 1-chloro-2-(β-chloroethoxy)butane, b.p. 195.5°, D_4^{20} = 1.1223, n_D^{20} = 1.453; the use of butene-2 or of 2-methylpropene (isobutylene) gives analogous products (283) cf. (284).]

Behavior of $\bar{C}$ with organometallic compounds (or their equivalents). [$\bar{C}$ with KC_6H_5 splits out KCl yielding (285) β-phenylethyl alc. (1:6505).]

$\bar{C}$ with arom. RMgX cpds. reacts in analogous fashion yielding the corresp. alcohols [e.g., $\bar{C}$ with C_6H_5MgBr (287) (288) or C_6H_5MgCl (289) gives (95% yield (286)) β-phenylethyl alc. (1:6505); $\bar{C}$ with *o*-tolyl MgBr gives (20–24% yield (290)) (287) β-(*o*-tolyl)-ethanol; $\bar{C}$ with *m*-tolyl MgBr gives (20–24% yield (290)) β-(*m*-tolyl)ethanol; $\bar{C}$ with *p*-tolyl MgBr gives (yields: 80% (291), 20–24% (290)) (287) β-(*p*-tolyl) ethanol; many other analogous cases are known].

[Note that $\bar{C}$ with C_2H_5MgBr gives (292) $ClCH_2CH_2OMgBr$ which may then be reacted with RMgBr types as above (292).]

[$\bar{C}$ with diethyl malonate in alc. NaOEt (i.e., diethyl disodiomalonate) might be expected to yield diethyl *bis*-(β-hydroxyethyl)malonate; this compd., however, is unknown since it loses 2 EtOH, ring-closing to (271) the spiro-dilactone of *bis*-(β-hydroxyethyl)malonic acid [Beil. XIX_1-(680)], m.p. 109–110°.] — [Note also that $\bar{C}$ (1 mole) with diethyl malonate (1 mole) + 1% HCl gas undergoes transesterification yielding (405) both β-chloroethyl ethyl malonate, b.p. 105–106° at 3 mm., and *bis*-(β-chloroethyl) malonate, b.p. 142–143° at 3 mm.]

[$\bar{C}$ with ethyl acetoacetate + alc. NaOEt (i.e., ethyl sodio-acetoacetate) boiled 5 hrs. gives a prod. (probably lactone of α-(β-hydroxyethylacetoacetic acid) which with 10% HCl after 5 hrs. boiling gives (40% yield (293)) pentanone-4-ol-1 (γ-aceto-*n*-propyl alc.) [Beil. I-831, I_1-(422), I_2-(873)], b.p. 115–116° at 20 mm. (294), D_4^{20} = 1.0071 (295), n_D^{20} = 1.439 (294) (corresp. semicarbazone, m.p. 167–168° (296)): note that this prod. (which is an important intermediate in the prepn. of the antimalarial "Atabrine" (297)) is best prepd. from ethylene oxide + ethyl sodioacetoacetate which gives first (60% yield (294)) the lactone of α-(β-hydroxyethyl)acetoacetic acid, b.p. 142–143° at 30 mm., n_D^{20} = 1.4562, which with warm HCl ring-opens and splits off AcOH giving (96% yield (294)) desired γ-aceto-*n*-propyl alc. (above).]

[$\bar{C}$ + sodium phenobarbital (Na deriv. of 5-ethyl-5-phenylbarbituric acid) gives (60% yield (298)) 1-(β-hydroxyethyl)phenobarbital, m.p. 145.0–145.5° cor. (note that this prod. is *not* obtd. from $\bar{C}$ + Ag salt of phenobarbital). — $\bar{C}$ with theobromine (3,7-dimethylxanthine) in aq. NaOH in s.t. at 125° for 6 hrs. gives (47–57% yield (366)) (367) 1-(β-hydroxyethyl)theobromine, m.p. 194° (367), 193° (366).]

Behavior of $\bar{C}$ with amines. *With primary aliphatic amines.* [$\bar{C}$ (1 mole) with aq. $MeNH_2$ (1 mole) at 110° for 12–24 hrs gives (80% yield (299)) β-(methylamino)ethanol [Beil. IV-276, IV_2-(718)], b.p. 159° (300) (301), 155–156° at 760 mm. (273) (corresp. 3,5-dinitrobenzoate, m.p. 195–196.5° (302); corresp. B.PkOH, 148° (303); corresp. reaction prod. with α-naphthyl isothiocyanate, viz., *N*-(β-hydroxyethyl)-*N*-methyl-*N'*-(α-naphthyl) thiourea, m.p. 125° (303)). — $\bar{C}$ with excess aq. $MeNH_2$ on standing in s.t. at 100° for several hrs. (304) or $\bar{C}$ with β-(methylamino)ethanol (above) in aq. at 120° (299) gives methyl-*bis*-(β-hydroxyethyl)amine (*N*-methyl-diethanolamine) [Beil. IV-284, IV_2-(729)], b.p. 115° at 5 mm. (240) (note that this prod. is new commercial chem. in U.S. (240)).]

[$\bar{C}$ with $EtNH_2$ as above should give β-(ethylamino)ethanol [Beil. IV-282, IV_2-(727)], b.p. 167–169° cor. at 751 mm., D_4^{20} = 0.914, n_D^{20} = 1.444, and (305) ethyl-*bis*-(β-hydroxyethyl)amine (*N*-ethyldiethanolamine) [Beil. IV-284], although both these prods. are usually prepd. from ethylene oxide.]

[For analogous reactn. of $\bar{C}$ with *n*-heptadecylamine yielding *N*-(β-hydroxyethyl)-*n*-

heptadecylamine see (306) (307); with cyclohexylamine yielding *N*-(β-hydroxyethyl)-cyclohexylamine see (308).]

With primary aromatic amines [C̄ (1 mole) with aniline (1 mole) refluxed a short time (299) (309) (310) (311) (312) (313) gives (yields: 70% (309), 40% (311)) *N*-(β-hydroxy-ethyl)aniline (β-phenylaminoethanol) [Beil. XII-182], b.p. 286° cor. (299), $n_D^{20} = 1.5749$ (317) (note that by reactn. of a second mole of C̄ some *N*,*N*-*bis*-(β-hydroxyethyl)aniline (see below) may also form, and that some *N*,*N'*-diphenylethylenediamine, m.p. 63.4–64.2°, may also appear (311)), note also that *N*-(β-hydroxyethyl)aniline on dehydration, e.g., by htg. in xylene with P_2O_5 (310), reacts bimolecularly giving in small yield *N*,*N'*-diphenylpiperazine, m.p. 160–162° (310) — C̄ (2 moles) with aniline (1 mole) especially in pres. of anhydr. Na_2CO_3 (310) or NaOH (314) or aq. at 110° (299) gives *N*,*N*-*bis*-(β-hydroxyethyl)aniline (*N*-phenyldiethanolamine) [Beil. XII-183, XII_1-(167)], m.p. 58° (315), 53.5–54° (310): note that this prod. on htg. at 200° under reduced press. (314) or htg. with P_2O_5 in xylene (310) or htg. with 70% H_2SO_4 at 160° (316) loses water and ring-closes to *N*-phenylmorpholine [Beil. XXVII-6], m.p. 53° (299), 52° (310).]

[C̄ (1 mole) with *o*-toluidine (2 moles) at 120–130° for several hrs. (318) (313) gives β-(*o*-tolylamino)ethanol, b.p. 172° at 12 mm. (318), 145–150° at 3 mm. (317), $n_D^{20} = 1.5675$ (317); note that in pres. of Na_2CO_3 the main (318) prod. (because of bimolecular condens. of this prod.) is *N*,*N'*-di-*o*-tolylpiperazine [Beil. XXIII-8], m.p. 174°. — C̄ with *p*-toluidine on htg. gives (319) β-(*p*-tolylamino)ethanol [Beil. XII-907], b.p. 177–178° at 14 mm. (319), m.p. 42–43° (317); note, however, that analogous bimolecular ring closure of this prod. readily occurs on htg. yielding (320) *N*,*N'*-di(*p*-tolyl)piperazine [Beil. XXIII-9], m.p. 190°.]

[C̄ with *o*-methoxyaniline (*o*-anisidine) at 100° for 48 hrs. gives (75–80% yield (321)) (299) β-(*o*-methoxyphenylamino)ethanol [Beil. XIII-367], b.p. 305° cor. (299) (corresp. B̄.HCl, m.p. 134°; B̄.PkOH, m.p. 140° (321)), note that this prod. with 5 pts. conc. HCl in s.t. at 160–180° gives by a remarkable elimination of MeOH and monomolecular ring closure (38% yield (321)) (299) "phenmorpholine" [Beil. XXVII-31], b.p. 268° cor. (299), 127–128° at 12 mm. (321). — C̄ with *p*-ethoxyaniline (*p*-phenetidine) gives on htg. (319) β-(*p*-ethoxyphenylamino)ethanol, m.p. 67°, b.p. 190° at 11 mm. (319) cf. (322).]

Many other cases, analogous to the above examples, are also known but cannot be included here.

With secondary aliphatic amines. Because of the great importance of β-(dialkylamino)-ethanols in the prepn. and study of physiologically active compounds, much study has been given to their prepn. from C̄ (and otherwise). From the resulting mass of data, the following examples are cited.

[C̄ with Me_2NH gives (323) β-(dimethylamino)ethanol [Beil. IV-276, IV_1-(425), IV_1-(719)], b.p. 135° cor. at 758 mm., $D_4^{20} = 0.8866$, $n_D^{20} = 1.4300$ (324) (corresp. *p*-nitrobenzoyl ester, m.p. 58° (325)). — C̄ with Et_2NH on htg. (326) under reflux for 8 hrs. (327) or in pres. of NaOH under press. at 160° for 3 hrs. (328) gives (yields: 83% (328), 68–70% (327)) β-(diethylamino)ethanol [Beil. IV-282, IV_1-(727)], b.p. 163° at 760 mm. (329), 160° at 741 mm., 100° at 80 mm., 96° at 73 mm., 55° at 10 mm. (330), 42–41° at 8 mm. (329); $D_{25}^{25} = 0.8801$ (329); $n_D^{25} = 1.4400$ (329), 1.4350 (330) (corresp. *N*-(*p*-nitrophenyl)carbamate, m.p. 59–60° cor. (329)).]

[C̄ with di-*n*-propylamine under reflux gives (70% yield (331)) β-(di-*n*-propylamino)-ethanol [Beil. IV-282], b.p. 90–92° at 22 mm. (331) (corresp. *p*-nitrobenzoyl ester hydrochloride, m.p. 133.5–134.5° (325)). — C̄ with di-*n*-butylamine on htg. gives (332) (333) β-(di-*n*-butylamino)ethanol, b.p. 225–230° at 760 mm., sl. dec. (332), 226–228° at 738 mm. (324), 90–91° at 7 mm. (333); $D_{20}^{20} = 0.8624$ (325); $n_D^{20} = 1.4444$ (325) (corresp. *p*-nitrobenzoyl ester hydrochloride, m.p. 92.5–93.5° (325) (332)). — C̄ with di-(*iso*butyl)amine

isocyanate but always by indirect means; note also that on short boilg. with aq. or alc. alk. it loses HCl and by ring closure yields 3-phenyloxazolidone [Beil. XXVII-136], lfts. from alc., m.p. 124° (272), 122° (309).]

Ⓓ *β*-Chloroethyl *N*-(*p*-bromophenyl)carbamate: pl. from lgr., m.p. 88–89° (400). [From $\bar{C}$ with *p*-bromobenzazide (400).]

Ⓓ *β*-Chloroethyl *N*-(*α*-naphthyl)carbamate [Beil. XII-1236]: m.p. 102–103° (373), 101° (391) (93), 100–101° (309). [From $\bar{C}$ with *α*-naphthyl isocyanate (391) (373); also from *β*-chloroethyl chloroformate (3:5780) with *α*-naphthylamine (309): note also that with dil. KOH (309) this prod. loses HCl ring-closing to 3-(*α*-naphthyl)-oxazolidone-2 [Beil. XXVII-136], m.p. 125° (309), while with conc. KOH it merely undergoes hydrolysis of chlorine yielding *N*-(*β*-hydroxyethyl)-*α*-naphthylamine, m.p. 52° (309).]

—— *β*-Chloroethyl *N*-(*β*-naphthyl)carbamate [Beil. XII-1292]: m.p. 98° (309). [Prepd. indirectly from *β*-chloroethyl chloroformate (3:5780) with *β*-naphthylamine (309); for behavior with dil. and conc. KOH analogous to preceding case see (309).]

Ⓓ *β*-Chloroethyl *N*-carbamidocarbamate (*β*-chloroethyl allophanate) [Beil. III$_2$-(56)]: m.p. 182.5° (392), 181–182° (388). [From $\bar{C}$ with vapors of isocyanic acid (392) or from *β*-chloroethyl chloroformate (3:5780) with urea (388).]

—— *N*-(*β*-hydroxyethyl)phthalimide = (*β*-(*N*-phthalimido)ethanol) [Beil. XXI-469, XXI$_1$-(368)]: m.p. 129.5° cor. (394), 127–128° (395), 126.5–127.5° (357), 126–127° (396), 125–126° (397) (note that m.p. given by (393) is incorrect). [From $\bar{C}$ with K phthalimide in s.t. at 150° for 4 hrs. (393): note that the m.p. of 88–89° reported by the only worker (393) using this method is not far from that (81° (395)) of *N*-(*β*-chloroethyl)phthalimide leaving some question as to which prod. was really obtd.]

Ⓓ *N*-(*β*-hydroxyethyl)tetrachlorophthalimide: m.p. 208–209° (398). [From $\bar{C}$ with K tetrachlorophthalimide in s.t. at 200° for 6 hrs. (398).]

—— *β*-Chloroethyl triphenylmethyl ether: m.p. 132° (399). [From $\bar{C}$ with *α*-bromotriphenylmethane (399).]

[illegible]

[illegible] Laszlo, *J. Am. Chem. Soc.* **49**, 2107 (1927). (6) Matejka, Jelinek, *J. chim. phys.* **34**, 611–614 (1937). (7) Timmermans, *Bull. soc. chim. Belg.* **36**, 507 (1927). (8) Timmermans, Martin, *J. chim. phys.* **25**, 444–445 (1928). (9) Smyth, Walls, *J. Am. Chem. Soc.* **54**, 2263, 2266 (1932). (10) Snyder, Gilbert, *Ind. Eng. Chem.* **34**, 1519–1521 (1942).

(11) Gomberg, *J. Am. Chem. Soc.* **41**, 1414–1431 (1919). (12) Wurtz, *Ann.* **110**, 125–128 (1859). (13) Mathews, *J. Am. Chem. Soc.* **48**, 570 (1926). (14) Suter, Oberg, *J. Am. Chem. Soc.* **56**, 677–679 (1934). (15) Norris, Mulliken, *J. Am. Chem. Soc.* **42**, 2095 (1920). (16) Smith, Boord, Adams, Pease, *J. Am. Chem. Soc.* **49**, 1338 (1927). (17) Kirner, *J. Am. Chem. Soc.* **48**, 2747–2753 (1926). (18) Winstrom, Warner, *J. Am. Chem. Soc.* **61**, 1205–1210 (1939). (19) Forster, Newman, *J. Chem. Soc.* **97**, 2573 (1910). (20) Street, Adkins, *J. Am. Chem. Soc.* **50**, 162–167 (1928).

(21) Timmermans, Mataar, *Bull. soc. chim. Belg.* **30**, 216 (1921). (22) Radulescu, Muresanu, *Bul. Soc. Stiinte Cluj* **7**, 129–153 (1932); *Cent.* **1933**, I 3156; *C.A.* **27**, 2085 (1933). (23) Bozza, [illegible] 162 (1931). [illegible] *C.A.* **14**, [illegible] in, Rivat, *Bull. soc. chim.* (4) **25**, 552–560 (1909). (27) Moureu, Brown, *Bull. soc. chim.* (4) **27**, 902–903 (1920). (28) Kirst (to Dow Chem. Co.), U.S. 1,386,118, Aug. 2, 1921; *Cent.* **1921**, IV 1065; *C.A.* **15**, 3851 (1921). (29) Ernst, Kaufler (to A. Wacker Soc. Elektrochem. Ind.), Ger. 486,492, Nov. 25, 1929; *Cent.* **1930**, I 2005; *C.A.* **24**, 1869 (1930). (30) Soc. Anon. des Distilleries des Deux Sèvres, Czechoslov. 34,718, Jan. 10, 1931; *Cent.* **1932**, II 2107; not in *C.A.*; Brit. 305,528, April 4, 1929; *Cent.* **1929**, II 485; *C.A.* **23**, 4712 (1929).

(31) Kaplan, Grishin, Skvortsova, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 538–544 (1937); *Cent.* **1937**, II 2332; *C.A.* **31**, 4554 (1937). (32) Kireev, Kaplan, Zlobin, *J. Applied Chem.* (*U.S.S.R.*) **7**,

1333–1338 (1934); *Cent.* **1936**, I 4286; *C.A.* **29**, 5712 (1935). (33) Faber, Miller, *Org. Syntheses*, Coll. Vol. **2**, 576–578 (1943); **12**, 68–70 (1932). (34) Forrester, U.S. 2,049,608, Aug. 4, 1936; *Cent.* **1937**, I 182; *C.A.* **30**, 6245 (1936). (35) Schmidt, Grossinsky (to I.G.), U.S. 1,882,978, Oct. 18, 1932; *Cent.* **1933**, I 2312; *C.A* **27**, 737 (1933): Brit. 309,025, Oct. 10, 1929; *Cent.* **1930**, II 304; *C.A.* **24**, 2468 (1930): French 650,972, Feb 13, 1929; *Cent.* **1933**, I 2312; *C.A.* **23**, 3231 (1929). (36) Ferris (to Atlantic Refining Co.), U.S 2,072,104, March 2, 1937; *Cent.* **1937**, I 4719, *C.A.* **31**, 2810 (1937). (37) Humphrey (to Hercules Powder Co.), U.S. 1,715,086, May 28, 1929; *Cent.* **1930**, I 294, [*C.A.* **23**, 3588 (1929)]. Canadian 284,988, Nov. 20, 1928; *C.A.* **23**, 1001 (1929); not in *Cent.* (38) Freudenberg, Acker, *Ber.* **71**, 1400–1406 (1941). (39) Schütz, *Cellulosechem.* **19**, 33–38 (1941), *C.A.* **36**, 5008 (1942). (40) B.A.S.F., Ger. 393,566, April 5, 1924; *Cent.* **1924**, II 120, not in *C.A.*

(41) Rosenthal (to F. Bayer Co), Ger. 383,699, Oct. 16, 1923, *Cent.* **1924**, I 252; not in *C.A.* (42) Webb (to Eastman Kodak Co), U S. 1,444,406, Feb 6, 1923, *Cent* **1923**, IV 342; *C.A.* **17**, 1329 (1923). (43) F. Bayer Co, Brit 209,333, Sept 10, 1924, *Cent.* **1924**, II 2715; not in *C.A.* (44) Smith, *Natl Inst. Health Bull.* **165**, 11–29 (1936), *Cent.* **1938**, I 2016; *C.A.* **30**, 4565 (1936). (45) Pratt, *Nature* **126**, 995 (1930). (46) Koelsch, *Zentr. Gewerbehyg. Unfallverhüt.* **14**, 316–325 (1927); *Cent.* **1927**, II 2467. (47) Clark, Edwards, *Trans Roy Soc. Can.* (3) **28**, III 107–125 (1934); *Cent.* **1935**, I 2548, *C A.* **29**, 1112 (1935). (48) Clark, Fowler, Black, *Trans. Roy. Soc. Can.* (3) **25**, III 99–105 (1931), *Cent.* **1933**, I 2708, *C A.* **26**, 2755 (1932). (49) Clark, Archibald, *Trans. Roy. Soc. Can* (3) **26**, III 87–92 (1932); *Cent.* **1933**, I 3951; *C.A.* **27**, 1649 (1933). (50) Schultz, Frey (to Standard Brands, Inc.), U S 1,893,152, Jan 3, 1933, *Cent.* **1933**, I 1862; *C.A.* **27**, 2249 (1933).

(51) Moureu, Dodé, *Bull. soc. chim.* (5) **4**, 281–295 (1937); *Compt. rend.* **203**, 802–804 (1936). (52) Frahm, *Rec. trav. chim.* **50**, 261–267 (1931). (53) Bozza, Mamoli, *Giorn. chim. ind. applicata* **12**, 283–292 (1930), *Cent.* **1930**, II 1854, *C.A.* **24**, 5021 (1930). (54) Brooks, *Chem. Met. Eng.* **22**, 629–633 (1920). (55) Shilov, Kanyaev, Domina, Ionina, *J. Phys Chem.* (*U.S.S.R.*) **13**, 1242–1248 (1939), *C.A* **35**, 371 (1941). (56) Zimakov, Gripich, *Org. Chem. Ind* (*U.S.S.R.*) **1**, 396–404 (1936), *Cent* **1937**, I 1012; *C A.* **30**, 6705 (1936). (57) Tropsch, Kassler, *Mitt. Kohlenforsch. Inst. Prag* **1931**, No. 1, 16–42, *Cent* **1932**, I 2159, *C.A* **26**, 1242 (1932). (58) Zapadinskii, *J. Chem. Ind.* (*Moscow*) **5**, 1426–1429 (1928); *C.A.* **23**, 3208 (1929), not in *Cent.* (59) Shilov, *J. Chem. Ind.* (*Moscow*) **5**, 1273–1276 (1928); *Cent* **1929**, II 1646; *C.A.* **23**, 2937 (1929). (60) Carius, *Ann.* **126**, 195–199 (1865), Butlerow, *Ann* **144**, 40–42 (1867)

(61) Britton, Nutting, Huscher (to Dow Chem Co.), U.S 2,130,226, Sept. 13, 1938; *Cent.* **1939**, I 1856, *C A.* **32**, 9096 (1938). (62) Youtz (to Standard Oil Co.), U.S. 1,875,309, Aug. 30, 1932; *Cent.* **1933**, II 2053, *C.A.* **26**, 5971 (1932) (63) Essex, Ward (to du Pont Co), U.S. 1,626,398, April 26, 1927; *Cent.* **1928**, I 410; *C.A.* **21**, 2136 (1927) (64) Essex, Ward (to du Pont Co), U S 1,594,608, Aug. 3, 1926; *Cent.* **1926**, II 1693, *C.A.* **20**, 3170 (1926). (65) McElroy, U.S. 1,510,790, Oct. 7, 1924, *C.A* **19**, 77 (1925), not in *Cent.* (66) Brooks, 1,498,781, 1,498,782, June 24, 1924; *Cent.* **1924**, II 1631, *C.A.* **18**, 2606 (1924). (67) Irvine, Haworth (to Carbide and Carbon Chem. Corpn), U.S. 1,496,675, June 3, 1924; *Cent* **1924**, II 1510; *C.A.* **18**, 2345 (1924). (68) Young, U.S 1,456,959, May 29, 1923; *C.A.* **17**, 2428 (1923); not in *Cent.* (69) Curme, Young, U.S. 1,456,916, May 29, 1923; *C.A.* **17**, 2428, not in *Cent.* (70) Eldred, U.S. 1,456,590, May 29, 1923, *C A* **17**, 2428, not in *Cent.*

(71) Brooks (to Chateloid Chem. Co.), U S. 1,394,664, Oct. 25, 1921; *Cent.* **1922**, IV 941; *C.A.* **16**, 423 (1922) (72) Finkelstein (to I.G.), Canadian 285,920, Dec. 25, 1928, *Cent.* **1932**, I 1153; *C.A* **23**, 1138 (1929) (73) Curme, Young, Canadian 238,729, March 18, 1924; *Cent.* **1925**, I 1129, not in *C.A.* (74) Kennedy, Barker (to Shawinigan Chem, Ltd.), Brit. 552,319, April 1, 1943; *C.A* **38**, 3992 (1944) (75) Soc. Carbochim., Brit. 445,011, April 30, 1936; *Cent.* **1936**, II 1244, [*C A.* **30**, 6390 (1936)] French 795,804, March 23, 1936; *C.A.* **30**, 5592 (1936); not in *Cent* (76) Tropsch, Kassler, Brit. 377,595, Aug. 18, 1932, *Cent.* **1932**, II 2724, [*C.A.* **27** 3944 (1933)] French 732,106, Feb. 17, 1932, *C.A.* **27**, 732 (1933), not in *Cent.* (77) Long, Willson, Wheeler, Brit. 265,269, March 3, 1927; *Cent.* **1927**, II 2350; *C.A.* **22**, 244 (1928). (78) Marks (to Carbide and Carbon Chem Corpn.), Brit. 235,044, July 2, 1925; *Cent.* **1928**, II 711; *C.A.* **20**, 917 (1926). Ger 537,940, June 24, 1931; *Cent* **1931**, II 1753; [*C.A.* **25**, 5177 (1931)] (79) T. Goldschmidt, A.G, Ger. 538,915, July 12, 1927, *C.A.* **26**, 2198 (1932); not in *Cent.*: Belgian 352,582, Jan. 8, 1929, *Cent.* **1931**, I 2932; not in *C.A.*: French 656,947, May 15, 1929; *Cent.* **1929**, II 648; [*C A* **23**, 4231 (1929)] Brit. 293,754, July 11, 1927; *C A.* **23**, 1651 (1929); not in *Cent.* (80) Union Chem Belg., French 829,493, June 28, 1938, *Cent.* **1938**, II 3316; *C.A.* **33**, 993 (1939).

(81) Comp. Prod Chim. d'Alais, etc., French 785,170, Aug. 3, 1935; *Cent.* **1936**, I 1309; *C A* **30**, 492 (1936). (82) Damiens, de Loisy, Piette, French 535,210, April 11, 1922, *Cent.* **1923**, II 741, not in *C A.* (83) Iskra, *J. Chem. Ind.* (*Moscow*) **12**, 947–953 (1935); *Cent.* **1936**, I 2823; *C.A.* **30**, 711 (1936). (84) Harford (to A. D. Little, Inc.), U.S. 2,107,789, Feb. 8, 1938; *Cent.*

(361) Meerwein, Hinz, *Ann.* **484**, 17, 22–23 (1930). (362) Fromm, Honold, *Ber.* **55**, 906–909 (1922). (363) Fromm, *Ann.* **442**, 130–140 (1925). (364) Ercoli, *Ann. chim. applicata* **25**, 263–273 (1935); *Cent.* **1935**, II 3090; *C.A.* **30**, 1028 (1936). (365) Yang, Johnson, *J. Am. Chem. Soc.* **54**, 2071 (1932). (366) Rojahn, Fegeler, *Arch. Pharm.* **268**, 568–569 (1930). (367) Béhal (to

Austrian 101,671, Nov. 25, 1925; *Cent.* **1926**, II 1585; not in *C.A.* (373) Jones, Burns, *J. Am. Chem. Soc.* **47**, 2973 (1925). (374) Blicke, Castro, *J. Am. Chem. Soc.* **63**, 2438 (1941). (375) Földi, *Ber.* **53**, 1837 (1920). (376) von Kereszty, Wolf, Ger. 353,105, May 12, 1922; *Cent.* **1922**, IV 156; *C.A.* **17**, 1243 (1923). (377) Gilman, Perkins, *J. Am. Chem. Soc.* **47**, 251 (1925). (378) Földi, *Ber.* **60**, 659 (1927). (379) Clemo, Perkin, *J. Chem. Soc.* **121**, 644 (1922). (380) Clemo, Tenniswood, *J. Chem. Soc.* **1931**, 2550.

(381) Tipson, Cretcher, *J. Am. Chem. Soc.* **64**, 1162 (1942). (382) Gilman, Beaber, *J. Am. Chem. Soc.* **45**, 841 (1923). (383) Perkin, Clemo (to British Dyestuffs Corp.), Brit. 193,618, March 22, 1923, *Cent.* **1925**, I 899; *C.A.* **17**, 3510 (1923). (384) Ashworth, Burkhardt, *J. Chem. Soc.* **1928**, 1798. (385) Johnson, Schwartz, Jacobs, *J. Am. Chem. Soc.* **60**, 1883 (1938). (386) Bert, *Compt. rend.* **213**, 1015–1016 (1941); *C.A.* **37**, 4049 (1943). (387) Puyal, Montagne, *Bull. soc. chim.* (4) **27**, 862 (1924). (388) von Kereszty, Wolf, Ger. 387,963, Jan. 7, 1924; *Cent.* **1924**, II 403, not in *C.A.* (389) Dewey, Witt, *Ind. Eng. Chem., Anal. Ed.* **14**, 648 (1942). (390) Sprinson, *J. Am. Chem. Soc.* **63**, 2250 (1941).

(391) Bickel, French, *J. Am Chem. Soc.* **48**, 749 (1926). (392) Grandière, *Bull. soc. chim.* (4) **35**, 189 (1924). (393) Dersin, *Ber.* **54**, 3158 (1921). (394) Smith, Platon, *Ber.* **55**, 3151 (1922). (395) Wenker, *J. Am. Chem. Soc.* **59**, 422 (19[illegible]
Soc. **65**, 762 (1943). (397) Garelli, Racciu, *Atti acca*[illegible]
I 358–363 (1934); *Cent.* **1934**, II 2823, [*C.A.* **29**, 622
Chem. Soc. **56**, 1409–1410 (1934). (399) Bennett,
(400) Sah, Tao, *Rec. trav. chim.* **58**, 14–15 (1939).

(401) Murray, *J. Council Sci. Ind. Research* **17**, 213–221 (1944); *C.A.* **39**, 2283 (1945). (402) Reed (to C. L. Horn) U.S. 2,378,104, June 12, 1945; *C.A.* **39**, 4088 (1945). (403) Goldblatt, Chiesman, *Brit. J. Ind. Med.* **1**, 207–213 (1944): Goldblatt, *Brit. J. Ind. Med.* **1**, 213–223 (1944): *C.A.* **39**, 5359 (1945). (404) Porret, *Helv. Chim. Acta*, **27**, 1321–1328 (1944); *C.A.* **39**, 4789 (1945). (405) Michael, Weiner, *J. Am. Chem. Soc.* **58**, 1003 (1936).

3:5555 1,1,1,2-TETRACHLOROETHANE $Cl.CH_2.CCl_3$
(Acetylidene tetrachloride)
(*unsym.*-Tetrachloroethane)

[For reactn. of C̄ with acetylene + cat. to yield 1,2-dichloroethylene (3:5030) with 1,1,2-trichloroethylene as by-product see (15); for reactn. of C̄ with 1,2-dichloroethylene + $AlCl_3$ to yield a pentachlorobutane, b.p. 76–77.9° at 10 mm., $D_{22}^{22} = 1.611$, $n_D^{22} = 1.5548$, see (16); for reactn. of C̄ with C_6H_5MgBr in toluene see (17).]

3:5555 (1) Henne, Hubbard, *J. Am. Chem. Soc.* **58**, 404–406 (1936). (2) Kharasch, Norton, Mayo, *J. Org. Chem.* **3**, 48–54 (1938). (3) Phillips, Davies, Mumford, *J. Chem. Soc.* **1929**, 548. (4) Mann, Pope, *J. Chem. Soc.* **121**, 597 (1922). (5) Nicodemus, *J. prakt. Chem.* (2) **83**, 318 (1911). (6) Parkhurst (to Stand. Oil Cal.), U.S. 1,948,015, Feb. 20, 1934; *Cent.* **1934**, II 863; *C.A.* **28**, 2021 (1934). (7) Kline (to du Pont Rayon), U.S. 2,042,944, June 2, 1936; *Cent.* **1937**, I 478; *C.A.* **30**, 5038 (1936). (8) Regnault, *Ann. chim.* (2) **69**, 162 (1838). (9) Laurent, *Ann.* **22**, 292–305 (1837). (10) I.G., Ger. 530,649, July 31, 1931, *Cent.* **1931**, II 1920.

(11) Kaufmann, *Ber.* **55**, 258 (1922). (12) Mouneyrat, *Bull. soc. chim.* (3) **19**, 499–500 (1898). (13) Kokatnur, *J. Am. Chem. Soc.* **41**, 122–123 (1919). (14) Prins, *Rec. trav. chim.* **45**, 80–81 (1926). (15) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; *Cent.* **1933**, I 1350; Ger. 567,272, Dec. 30, 1932; *Cent.* **1933**, I 1842. (16) Prins, *Rec. trav. chim.* **56**, 123–124 (1937). (17) Bert, *Bull. soc. chim.* (4) **41**, 1173–1174 (1927).

3:5570 *dl*-α-CHLORO-*n*-BUTYRYL CHLORIDE $C_4H_6OCl_2$ Beil. II - 277, II_1-(123), II_2—

$CH_3.CH_2.CH(Cl).C(Cl){=}O$

B.P. 129–132° (1)
62–63° at 70 mm. (2)
51–52° at 41 mm. (2)

$D_{\_}^{17} = 1.257$ (1)

[For prepn. of C̄ from α-chloro-*n*-butyric acid (3:9130) with $SOCl_2$ see (2); for formn. of C̄ from *n*-butyryl chloride (3:7370) with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (15% C̄ + 55% β- and 30% γ-isomers) see (3).]

C̄ on hydrolysis with aq. yields α-chloro-*n*-butyric acid (3:9130) q.v.

3:5570 (1) Markownikow, *Ann.* **153**, 241 (1870). (2) Blaise, *Bull. soc. chim.* (4) **15**, 668 (1914). (3) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940).

3:5576 β-CHLOROPROPIONALDEHYDE C_3H_5OCl Beil. I - 632, I_1—, I_2-(690)
(3-Chloropropanal-1, acrolein hydrochloride)

$CH_2(Cl).CH_2.CHO$

B.P. 130–131° (1)
125–130° (2)
50° at 60 mm. (3)
40–41° at 18 mm. (4)
40° at 19 mm. (1)
40–50° at 10 mm. (2)

$D_{\_}^{15} = 1.268$ (1) $n_{\_}^{15} = 1.475$ (1)

Liquid, insol. aq., sol. alc. or ether. — C̄ readily polymerizes (see below).

PREPARATION OF C̄

[For prepn. of C̄ from acrolein (1:0115) with dry HCl gas at −10 to −15° (yields: 87% (3), 65% (4)) (6) (7) (8) (9) (10) see indic. refs.; note that since HCl is present much of the prod. may appear as the trimer (see below); for prepn. of C̄ from its trimer (see below) by distillation at ord. press. see (1); for prepn. of C̄ from 1,3-dichloropropene-1 (3:5280) by cat. vapor-phase hydration see (20).]

tives) formerly (4) regarded as *cis* and *trans* stereoisomers of $\bar{C}$ may very probably be $\bar{C}$ and its synionic isomer (3:7480).

[For prepn. of $\bar{C}$ from 1,2,3-trichloro-2-methylpropane (3:5885) by dehydrochlorination with quinoline (73–85% yield) see (7).]

[For prepn. of $\bar{C}$ from 1,1-dichloro-2-methylpropene-2 (3:7480) by htg. under reflux see (2): for formn. of $\bar{C}$ (together with other products) from 2-methylpropene-1 (isobutylene) (60% yield (5)) (1) + Cl_2, or from 3-chloro-2-methylpropene-1 (isobutenyl chloride) (3:7145) with Cl_2 (1 mole) + $NaHCO_3$ (1.5 moles) at 0° (2) see indic. refs.; for formn. of $\bar{C}$ (20% yield (6)) (together with other products) from 1,3-dichloro-2-methylpropanol-2 (3:5977) + strong oxygen acids see (6); for formn. of $\bar{C}$ (46% yield (3)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by htg. with P_2O_5 for 2 hrs. at 110–115° see (3).]

$\bar{C}$ on hydrolysis with aq. + $CaCO_3$ (2) (4) or aq. + MgO (4) gives (2) (3) (46% yield (4)) 1-chloro-2-methylpropen-1-ol-3 (3-chloro-2-methylallyl alc.) (3:8340) q.v.

$\bar{C}$ with O_3 followed by hydrolysis yields (2) (3) (5) chloroacetone (3:5425).

$\bar{C}$ treated with Cl_2 in the dark at 0° for 37 hrs. yields (4) 1,1,2,3-tetrachloro-2-methylpropane (3·6165) + other products.

$\bar{C}$ with cuprous cyanide refluxed 9–10 hrs. gives (67% yield (7)) 4-chloro-3-methylbuten-3-nitrile-1, b.p. 70–73° at 10 mm., $D_4^{20} = 1.0856$, $n_D^{20} = 1.4643$ (7); this product on hydrolysis with hot conc. HCl for 2 hrs. gives (7) 4-chloro-3-methylbuten-3-oic acid-1, m.p. 35° (corresp. phenylhydrazide, m.p. 147–148°).

3:5590 (1) Pogorshelski, *J. Russ. Phys.-Chem Soc.* **36**, 1129–1184 (1904); *Cent.* **1905**, I 668, (2) Tishchenko, *J. Gen. Chem.* (*U.S S.R.*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4223; *C.A.* **33**, 4190 (1939). (3) D'yakonov, *J. Gen. Chem.* [illegible] **10** [illegible]
(4) Rogers, Nelson, *J. Am. Chem. Soc.* **58** [illegible]
J Gen. Chem. (*U.S.S.R.*) **9**, 1258–1264 (1939 [illegible]
Development Co.), U.S. 2,042,223, 2,042,222, May 26, 1936; *Cent.* **1937**, 1274; *C.A.* **30**, 4875 (1936). (7) Mooradian, Cloke, *J. Am. Chem. Soc.* **68**, 785–789 (1946).

3:5605 3,3,3-TRICHLORO-2-METHYLPROPENE-1 $C_4H_5Cl_3$ Beil. S.N. 11

(1,1,1-Trichloro-2-methylpropene-2)

$$\begin{array}{c} CH_3 \\ | \\ H_2C{=}C{-}CCl_3 \end{array}$$

B.P. 132° (1) $D_{-}^{20} = \mathbf{1.293}$ **(1)** $n_{-}^{20} = \mathit{1.479}$ *(1)*

Note: $\bar{C}$ readily undergoes allylic transposition so that in reactns. of $\bar{C}$ products derived from the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) may be expected (1) (2) (3) (4).

[For prepn. of $\bar{C}$ (yield: 30–43% (4), 15% (1)) from β,β,β-trichloro-*ter*-butyl alc. ("Chloretone") (3:2662) by htg. to 200° with P_2O_5 and dimethylaniline (1) or quinoline (4) see indic. refs.] [A 57% yield of the isomeric 1,1,3-trichloro-2-methylpropene-1 (3:5025) together with some α-chloroisobutyric acid (3:0235) is separated from $\bar{C}$ by redistillation (1).]

$\bar{C}$ on hydrolysis by boilg. 1 day with aq. Na_3PO_4 gives (60% yield (2)) 3,3-dichloro-2-methylpropen-2-ol-1, b.p. 78–79°, $D_{-}^{20} = 1.298$, $n_{-}^{20} = 1.493$ (*p*-nitrobenzoate, m.p. 91°, *N*-phenylcarbamate, m.p. 64° (2)).

$\bar{C}$ on htg. with NaOAc + AcOH gives (2) 3,3-dichloro-2-methylpropen-2-yl acetate, b.p. 79° at 12 mm., $D_{-}^{20} = 1.257$, $n_{-}^{20} = 1.4718$ (2). [With boilg. NaOH this regenerates the corresp. alc. (2).]

$\bar{C}$ with NaOEt gives in the cold 70% yield (2) of 3,3-dichloro-2-methylpropen-2-yl ethyl ether, b.p. 56° at 12 mm., $D_{-}^{20} = 1.1285$, $n_{-}^{20} = 1.4610$ (2).

C̃ in AcOH treated with O_3, then hydrolyzed, gives (70% yield) α,α,α-trichloroacetone (3:5620), b.p. 133–134° (1).

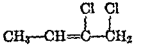
[For behavior of C̃ with PCl_5, with HF, or with HF + anisole see (4).]

Ⓓ **2,3-Dibromo-1,1,1-trichloro-2-methylpropane:** m.p. 34° (1). [From C̃ + Br_2 without solvent; crude prod. recrystd. from alc. at −10° (1); cf., however, (4).]

Ⓓ **3,3-Dichloro-2-methylpropen-2-yl *p*-nitrobenzoate:** m.p. 91° (2). [From C̃ on boilg. with dil. alc. soln. of K *p*-nitrobenzoate (2).]

3:5605 (1) Jacob, *Bull soc chim.* (5) **7**, 581–586 (1940). (2) Kirrmann, Jacob, *Bull. soc. chim.* (5) **7**, 586–593 (1940). (3) Kirrmann, Jacob, *Compt. rend.* **203**, 1528–1529 (1936). (4) Price, Marshall, *J. Org. Chem.* **8**, 532–535 (1943)

3:5615 1,2-DICHLOROBUTENE-2 (high-boilg. stereoisomer) $C_4H_6Cl_2$ Beil. S.N. 11



B.P. 132–134° at 762 mm.	(1)	D_4^{20} = **1.1597**	(2)	n_D^{20} = **1.4590**	(2)
125–127°	(2)	D_4^{18} = **1.1601**	(2)	n_C^{18} = **1.4635**	(2)
		D_4^{16} = **1.1771**	(1)	n_C^{16} = **1.4710**	(1)

[*See also low-boilg. stereoisomer* (3:5360).]

[For prepn. of C̃ (together with its stereoisomer (3:5360)) from 1,2,3-trichlorobutane (3:5935) with KOH at 150° (2), or from 2,2-dichlorobutane (3:7415) or 2,3-dichlorobutane (3:7615) with alc. KOH (5), see indic. refs.; for formn of C̃ (together with its stereoisomer and also 2,4-dichlorobutene-2 (3:5550)) from 2-chlorobutene-2 (3:7105) by actn. of Cl_2 at 350° see (3).]

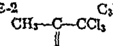
C̃ with 1 mole Cl_2 + 1.5 moles $NaHCO_3$ at 0° gives (100% yield (4)) 1,2,2,3-tetrachlorobutane (3:9078).

C̃ on hydrolysis by htg. with 2 pts. aq. + 1 mole powdered $CaCO_3$ at 70° for 4 hrs. gives (1) a mixt. of about equal parts of 2-chlorobuten-2-ol-1 (3:8240) and (by allylic transposition) 3-chlorobuten-3-ol-2 (3:9115).

C̃ on oxidn. with $KMnO_4$ in acetone gives (1) chloroacetic acid (3:1370) + AcOH (1:1010) + HCl. — C̃ in CCl_4 at −17° treated with O_3 followed by aq. gives acetaldehyde (1:0100).

3:5615 (1) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 658–662 (1937); *Cent* **1937**, II 371; *C.A.* **31**, 5754 (1937). (2) Tishchenko, Churbakov, *J. Gen Chem.* (*U.S.S R*) **6**, 1553–1558 (1936); *Cent.* **1937**, I 3786; *C A.* **31**, 2165 (1937). (3) N. V. Bataafsche Petroleum Maatschappij, Brit. 468,016, July 22, 1937, French 810,112, Mar. 15, 1937; *Cent.* **1937**, II 4102. (4) Tishchenko, *J. Gen. Chem.* (*U S S.R*) **8**, 1232–1246 (1938); *Cent.* **1939**, II 4222; *C A.* **33**, 4190 (1939). (5) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S R.*) **7**, 663–666 (1937); *Cent.* **1937**, II 371; *C.A.* **31**, 5754 (1937).

3:5620 1,1,1-TRICHLOROPROPANONE-2 (α,α,α-Trichloroacetone; methyl trichloromethyl ketone) $C_3H_3OCl_3$ Beil. I - 655, I_1-(344), I_2-(710)



B.P. 134°	(1) (3)	D_4^{20} = **1.435**	(3)	n_α^{20} = **1.4592**	(3)
133–134°	(2)	$D_4^{17.1}$ = **1.4389**	(3)		
60° at 54 mm.	(1)				
57° at 48 mm.	(1)				
27.5–28° at 10 mm.	(3)				

Limpid colorless liq. with faintly camphoraceous odor. — Insol. aq., but volatile with steam (3). — C̃ is not lachrymatory.

[For prepn. from 1,1,1-trichloro-2-methylpropene-2 (3:5605) with O_3 in AcOH, followed by hydrolysis (70% yield) see (2); from corresp. alc., 1,1,1-trichloropropanol-2 (3:0846), by oxidn. with $K_2Cr_2O_7/H_2SO_4$ see (3); from 2-trichloromethyl-2,4,4-trimethyl-1,3-dioxolone-5 [Beil. XIX_1-(656)] by hydrolytic cleavage with AcOH/HCl (60% yield) see (1): for formn. of Č (together with other prods.) from propanol-2 (1:6135) with Cl_2 (4), from chloroacetone (3:5425) with Cl_2 at 30–40° (5), or from trichloroacetyl chloride (3:5420) with MeZnI (1) see indic. refs. — Note that the prod. from chloral + diazomethane, formerly supposed (6) to have been Č, has since been shown (7) (8) to be 3,3,3-trichloro-1,2-epoxypropane (3:5760) ("γ,γ,γ-trichloropropylene oxide").]

[Č on reduction with $Al(C_2H_5)_3.Et_2O$ in ether (9) or with fused $Al(OEt)_3$ in abs. alc. under H_2 or N_2 (10) gives (yields: 67% (10), 65% (9)) 1,1,1-trichloropropanol-2 (3:0846).]

[Č resists further chlorination; e.g., Č with SO_2Cl_2 (1 mole) on protracted htg. at 180° yields (3) 1,1,1,3-tetrachloropropanone-2 (3:6085), b.p. 71–72° at 13 mm., hydrate, m.p. 65° (3).]

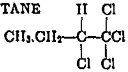
[Č with diazomethane in dry ether gives (83% yield (3)) 1,1,1-trichloro-2-methyl-2,3-epoxypropane, b.p. 51° at 10 mm., m.p. 53–54° (3).]

Ⓟ Cleavage with aq. alkali: Č with aq. alk. even in cold splits almost instantly (1) (2) into chloroform (3:5050) and acetic acid (1:1010).

Ⓓ **1,1,1-Trichloropropanone-2 semicarbazone:** m.p. 140° dec. (on Hg bath) (1) (11). [From Č with semicarbazide HCl in pres. of NaOAc, or with free semicarbazide (11).]

3:5620 (1) Blaise, *Bull. soc. chim.* (4) **15**, 731–737 (1914); *Compt. rend.* **155**, 1253 (1912). (2) Jacob, *Bull. soc. chim.* (5 … ionde, Ender, *Monatsh.* **59**, 214–216 (1 … pt. 27, 1921; *Cent.* **1922**, IV 912. (5) … (6) Schlotterbeck, *Ber.* **42**, 2561–256 … (8) Arndt, *Z. angew. Chem.* **40**, 1099–1100 (1927). (9) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) **147**, 236–237 (1936). (10) Meerwein, Schmidt, *Ann.* **444**, 233–234 (1925). (11) Blaise, *Bull. soc. chim.* (4) **17**, 428 (1915); *Compt. rend.* **156**, 1551 (1913)

3:5622 1,1,1,2-TETRACHLOROBUTANE $C_4H_6Cl_4$ Beil. S.N. 10

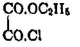


B.P. 134–135° at 742 mm. (1) D^{20}_{20} = **1.3932 (1)** n^{25}_D = **1.4920 (1)**

[For prepn. of Č from 1,1,1-trichlorobutanol-2 (3:5955) with conc. HCl + $ZnCl_2$ on stdg. at room temp. 1 hr. (yield not stated) see (1).]

3:5622 (1) Gilman, Abbott, *J. Org. Chem.* **8**, 228 (1943).

3:5625 ETHOXALYL CHLORIDE $C_4H_5O_3Cl$ Beil. II - 541, II_1-(234), II_2-(508)



B.P. 136–138°	(1)	D^{20}_4 = 1.2231	(2)
135–136°	(2)	1.2226	(3)
135°	(3)		
134–135°	(4)		
133–135° at 760 mm.	(14)		
30° at 10 mm.	(2)		

Colorless mobile liq. with penetrating odor. — $\bar{C}$ fumes in air and gradually deposits hydrated oxalic acid (1:0445) (17). — $\bar{C}$ as such is insol. in aq. but rapidly hydrolyzes with formn. of HCl and ethyl hydrogen oxalate, the latter in turn being converted to oxalic acid (1:0445) + EtOH.

[For prepn. of $\bar{C}$ from diethyl oxalate (1:1055) with PCl_5 (yields: 80–90% (5), 84% (6), 80% (7)) (8) (9) (10) (11) (34) see indic. refs.; note that this mode of prepn. has been shown (4) to comprise two distinct and successive reactions: first the formn. of ethyl α,α-dichloro-α-ethoxyacetate, $Cl_2C(OEt).COOEt$ [Beil. II-543, II_1-(236)], b.p. abt. 85° at 10 mm., D_4^{20} = 1.23155 (2); and second, the pyrolysis of this product by repeated distillation (13) or increased temp. (especially in the pres. of catalysts such as salts of Fe or Pt (5) (12)) yielding $\bar{C}$ + ethyl chloride (3:7015).]

[For prepn. of $\bar{C}$ from ethyl hydrogen oxalate [Beil. II-535, II_1-(232), II_2-(504)] with $SOCl_2$ (yields: 78% (14), 72% (15)) or with PCl_5 (3) see indic. refs. (note that the initial ethyl hydrogen oxalate is readily obtd. from anhydrous oxalic acid (1:0535) with diethyl oxalate (1:1055) by htg. 3 hrs. (32% yield (15)) (18) or by distn. with EtOH and CCl_4 as directed (61% yield (16))); for prepn. of $\bar{C}$ from K ethyl oxalate with $POCl_3$ or PCl_5 (17) (3) or with $SOCl_2$ (60–70% yield (24)) see indic. refs. (note that K ethyl oxalate can readily be prepd. in 95–97% yield from diethyl oxalate (1:1055) by digestion with aq. KOAc (24)).]

[For prepn. of $\bar{C}$ from oxalyl (di)chloride (3:5060) with EtOH (1:6130) by reactn. of one acid chloride group but not the other (60% yield) see (25).]

[$\bar{C}$ on passing through tube at 200° loses CO yielding (19) ethyl chloroformate (3:7295).]

[$\bar{C}$ with EtOH (1:6130) reacts normally yielding (17) diethyl oxalate (1:1055); for reactn. of $\bar{C}$ with cellulose see (25).]

[$\bar{C}$ with diethyl sodiomalonate in ether gives (20) (12) a mixt. of triethyl oxalomalonate [Beil. III-850, III_1-(292)] and tetraethyl dioxalomalonate [Beil. III_2-(199)]; $\bar{C}$ with ethyl sodio-cyanoacetate in ether gives (21) (22) diethyl oxalo-cyanoacetate [Beil. III-850], m.p. 98° (22), 96° (21); $\bar{C}$ with diethyl methyl sodio-malonate gives (23) diethyl oxalo-methyl-malonate; many other analogous condensations cannot be included here.]

[$\bar{C}$ with aromatic hydrocarbons in the pres. of $AlCl_3$ undergoes reactn. of the Friedel-Crafts type, and this procedure has been widely studied as a means of introduction of the —CO.COOEt group: e.g., $\bar{C}$ with C_6H_6 + $AlCl_3$ in nitrobenzene + CS_2 gives (26) ethyl benzoylformate (ethyl phenylglyoxylate) [Beil. X-657, X_1-(314)], b.p. 256–257°; for corresp. analogous reactn. with toluene (1:7405) (27), *m*-xylene (1:7420) (27), cumene (1:7440) (9), pseudocumene (1:7470) (27), or mesitylene (1:7455) (27) (1) see indic. refs.]

$\bar{C}$ with NH_3 in alc. gives (17) ethyl oxamate, $NH_2.CO.CO.OC_2H_5$ [Beil. II-544, II_1-(236), II_2-(509)], lfts. from hot alc., m.p. 114°. — Similarly $\bar{C}$ with aniline should yield ethyl oxanilate, $C_6H_5.NH.CO.CO.OC_2H_5$ [Beil. XII-282, XII_1-(206)], tbls. or pr. from alc., ndls. from hot aq., m.p. 66–67°; $\bar{C}$ with phenylhydrazine should yield β-(ethoxalyl)-phenylhydrazine, $C_6H_5.NH.NH.CO.CO.OC_2H_5$ [Beil. XV-264], lfts. from alc., m.p. 119°.

$\bar{C}$ with urea (2 moles) reacts vigorously at room temp. as a normal acid chloride yielding (28) ethyl oxalurate, $NH_2.CO.NH.CO.CO.OC_2H_5$ [Beil. III-65, III_2-(54)], ndls. from ether, m.p. 184–185°.— Note, however, that $\bar{C}$ with *N*-phenylurea on htg. evolves CO + C_2H_5Cl (3:7015) and yields (29) a mixt. of ethyl ω-phenylallophanate, $C_6H_5.NH.CO.NH.COOC_2H_5$ [Beil. XII-359, XII_1-(234)], ndls. from boilg. alc., m.p. 106° (30), and *N*-phenyl-parabanic acid (oxalyl *N*-phenylurea) [Beil. XXIV-454, $XXIV_1$-(405)], lfts. from alc., m.p. 208° (29). — $\bar{C}$ with *N,N'*-diphenylurea in C_6H_6 on htg evolves C_2H_5Cl (3:7015) and yields (29) *N,N'*-diphenylparabanic acid (oxalyl *N,N'*-diphenylurea) [Beil. XXIV-455, $XXIV_1$-(405)], ndls. from alc., m.p. 204°. — $\bar{C}$ with *N,N'*-dimethylurea (2 moles)

reacts vigorously giving (80% yield (31)) N,N'-dimethylparabanic acid [Beil. XXIV-453, $XXIV_1$-(404)], m.p. 154°.

[$\bar{C}$ with RMgX cpds. gives (32) disubstituted glycolic acids ($R_2C(OH)COOH$) and/or ethoxalyl esters of disubstituted ethyl glycolates, $R_2C(O.CO.COOC_2H_5)$ $(COOC_2H_5)$; similarly $\bar{C}$ with diethylcadmium gives (63% yields (33)) ethyl α-ethyl-α-hydroxy-*n*-butyrate (ethyl α,α-diethylglycolate).]

(2) Anschütz, *Ann.* **254**, 20, 27 (1889). (3) Mol, 2160 (1886). (5) Blaise, *Bull.* 47–49 (1927). (7) Bert, *Bull.* –2160 (1886). (9) Bert, *Bull.* 373–378 (1905). (12) Scholl, Egerer, *Ann.* **397**, 678 (1928). (14) Diels, Naw- *ll. soc. chim.* (4) **41**, 537–540 (1927). (16) Contzen-Crewet, *Bull. soc. chim. Belg.* **35**, 167–170 (1926). (17) Henry, *Ber.* **4**, 599–601 (1871). (18) Fourneau, Sabetay, *Bull. soc. chim.* (4) **43**, 860 (1928). (19) Grassi, *Gazz. chim. ital.* **27**, I 31–32 (1897). (20) von Auwers, Auffenberg, *Ber.* **51**, 1103–1106 (1918). (22) Bertini, *Gazz. chim. ital.* **31**, I Adickes, Brun- *Ber.* **63**, 1532- 6 (1897). (27) 3 (1871). (29) 345–346 (1897). 948–953 (1903). 8,532, Oct. 29, 1942; *C.A.* **38**, 378 (1944).

3:5630 1,1,2-TRICHLOROPROPANE $CH_3.CH(Cl).CHCl_2$ $C_3H_5Cl_3$ Beil. I-106
(α-Chloropropylidene (di)- chloride) I_1— I_2—

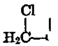
B.P. 135–137° (1) cf. (2) $D^{16}_{-} = $ **1.353** (1)
132° (3)

[For prepn. from 1,2-dichloropropane (propylene dichloride) (3:5200) by chlorination in presence of iron and ultra-violet light at 10–40°, or without ultra-violet light above 50°, see (4), or with SO_2Cl_2 in pres. of organic peroxides see (6) (7).]

$\bar{C}$ htd. with aq. or alc. alk. splits out HCl yielding (5) 1,1– (3:5120), b.p. 78°.

Bull. soc. chim. (3) **21**, 620 (1899). (2) V *chim.* 3). (4) Levine, C 471 (to du Pont), 30, *Chem. Soc.* **61**, 27, 1945; *C.A.*

3:5633 3-CHLORO-2-(PROPENE-1
(1-Chloro-2-(chlorome γ,γ-dichloroisobutylene) I I_1



B.P.		M.P.
138–138.3°	(9)	−15°
30–31° at 9 mm.	(1)	

Colorless oil with faintly halogen-

[For prepn. of C̄ from *tris*-(chloromethyl)acetic acid (itself obtd. in quant. yield by conc. HNO_3 oxidn. (9) of 3-chloro-2,2-*bis*-(chloromethyl)propanol-1 = pentaerythrityl trichlorohydrin (9)) by combine decarboxylation and dehydrochlorination in boilg. quinoline (75–85% yield) see (9).]

[For formn. of C̄ (*40% yield (2) together with other products (2) (3)) from* 2-methylpropene-1 (isobutylene) with Cl_2 (2) (3) or from 3-chloro-2-methylpropene-1 (isobutenyl chloride) (3:7145) with Cl_2 (1 mole) + $NaHCO_3$ (1.5 moles) at 0° see (2) (4) see indic. refs.; for formn. of C̄ (together with other products) from 1,2,3-trichloro-2-methylpropane (3:5885) by pyrolysis at 450–550° see (5); *for formn. of* C̄ (together with 1,3-dichloro-2-(chloromethyl)propene-1 (3:9066)) from 1,3-dichloro-2-nitro-2-(chloromethyl)propane with Na/Hg see (1); for prepn. of C̄ (80% yield (6) together with 20% yield 1,3-dichloro-2-methylpropene-1 (3:5590)) from 1,3-dichloro-2-methylpropanol-2 (3:5977) by actn. of strong oxygen acids see (6).]

C̄ on cat. hydrogenation using Pt black yields (1) 1,3-dichloro-2-methylpropane (3:7960), but C̄ in alc. on boilg. with Zn dust gives (75% yield (3)) isobutylene, b.p. −6°.

C̄ with O_3 gives (2) α,α'-dichloroacetone (3:0563).

C̄ treated with Cl_2 in the dark at 0° yields (5) *1,2,3-trichloro-2-chloromethylpropane* (3:6335). — C̄ treated with Br_2 in $CHCl_3$ yields (1) 1,2-dibromo-3-chloro-2-(chloromethyl)-propane, colorless odorless oil, b.p. 140° at 10 mm. (1); note, however, failure to react with Br_2 recorded later (9).

C̄ with aq. alk. as specified (7) yields 2,3-epoxy-2-chloromethylpropanol-1, b.p. 85° at 1 mm. (7). [For similar reactns. cf. (8).]

C̄ on hydrolysis with aq. $CaCO_3$ refluxed 2 hrs. gives (36% yield (9)) 2-(hydroxymethyl) propen-2-ol-1, b.p. 125–126° at 18 mm., $D_4^{20} = 1.0791$, $n_D^{20} = 1.4758$ (9).

3:5633 (1) Kleinfeller, *Ber.* **62**, 1595 (1929). (2) D'yakonov, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1258–1264 (1939), *C.A.* **34**, 710 (1940). (3) D'yakonov, *J. Gen. Chem.* (*U.S.S.R.*) **10**, 402–413 (1940), *C.A.* **34**, 7861 (1940). (4) Engs, Groll, Fairbairn (to Shell Development Co.), U.S. 2,189,890, Feb. 13, 1940; *C.A.* **34**, 4079 (1940). (5) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1029–1031 (1936). (6) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, U.S. 2,042,222, May 26, 1936, *Cent.* **1937**, I 1274, *C.A.* **30**, 4875 (1936). (7) Groll, Hearne (to Shell Development Co.), U.S. 2,070,990, Feb. 16, 1937; *Cent.* **1937**, II 2133, *C.A.* **31**, 2612 (1937). (8) Hearne, de Jong, *Ind. Eng. Chem.* **33**, 940–943 (1941). (9) Mooradian, Cloke, *J. Am. Chem. Soc.* **67**, 942–944 (1945).

3:5635 2-CHLOROPROPEN-2-OL-1 (2-Chloropropen-1-ol-3; β-chloroallyl alcohol)

$CH_2{=}C(Cl){-}CH_2OH$ C_3H_5OCl

Beil. I-439
I_1—
I_2—

B.P. 130–140° *cor.* (1)
136° (2)

$D_{\ }^{\ } = $ **1.164 (2)**

Note that C̄ *is the true* β*-chloroallyl alcohol*; care must be taken to avoid confusion with 3-chloropropen-2-ol-1 (γ-chloroallyl alcohol) (3:5820) whose derivatives have often been designated in the literature as β-chloroallyl derivatives; see also the warning note under γ-chloroallyl chloride (3:5280).

[*For prepn. of* C̄ *from 2,3-dichloropropene-1* (3:5190) by hydrolysis of the reactive halogen atom with hot dil. aq. alk. see (2); from 2-chloro-3-iodopropene-1 by hydrolysis of the iodine atom with hot dil. aq. KOH or with silver oxide see (1); from butadiene-1,2-(allene) with HOCl see (3).]

Colorless liq. with faint odor; C̄ does not have the violent vesicant action on skin shown by the isomeric γ-chloroallyl alc. (3:5820).

C̄ readily dissolves in conc. H_2SO_4 with evolution of HCl gas; after pouring onto ice and distilling acetol (hydroxyacetone) (1:5455) is obtd. (2).

[C̄ with PBr_3 yields (2) 3-bromo-2-chloropropene-1 (β-chloroallyl bromide) [Beil. I-201, I_1-(171)], b.p. 121° (2), 119–120° (4).]

[C̄ yields by suitable treatment (no details (2)) β-chloroallyl acetate [Beil. II-136], b.p. 145° (2). — For esters of C̄ with monocarboxylic acids (5), saturated polycarboxylic acids (6), and halogenated acids (7), and for copolymerization of certain esters of C̄ with styrene (8) see indic. refs.]

3:5635 (1) van Romburgh, *Rec. trav. chim.* **1**, 238 (1882). (2) Henry, *Bull. soc. chim.* (2) **39**, 526 (1883). (3) Smirnov, *J. Russ. Phys.-Chem. Soc.* **35**, 854–872 (1903); *Cent.* **1904**, I 576. (4) von Braun, Kühn, Weismantel, *Ann.* **449**, 250 (1926). (5) Coleman, Hadler (to Dow Chem. Co.), U.S. 2,208,960, July 23, [illegible] Co., U.S. 2,159,008, May 23, [illegible] Dow Chem. Co.), U.S. 2,221 [illegible] Zemba (to Dow Chem. Co.), [illegible]

3:5640 α,β-DICHLORODIETHYL ETHER

$C_4H_8OCl_2$ — Beil. I - 612, I_1-(328), I_2-(676)

(α,β-Dichloroethyl ethyl ether)

$$\underset{\text{Cl}}{CH_2}.\underset{\text{Cl}}{CH}.O.CH_2.CH_3$$

B.P. 140–145° (1) (2)
132–133° at 725 mm. (3)
66–69° at 45 mm. (4)
36–37° at 15 mm. (3)

$D^{23}_{23} = 1.174$ (1)

Colorless liq. with sharp odor.

[For prepn. from diethyl ether (1:6110) by chlorination see (4) (1).]

C̄ with cold aq. rapidly hydrolyzes yielding chloroacetaldehyde hydrate (3:7212), ethyl alc. (1:6130), and HCl; for study of rate at 20° see (6).

C̄ in dil. alc. htd. some hrs. at 60° with $NH_2OH.HCl$ (3 moles) + KOH (5 moles) soln. evapd., acidified with dil. H_2SO_4, extracted with ether, ether soln. dried with $CaCl_2$, evapd. gives (40% yield (5)) glyoxal dioxime (glyoxime) [Beil. I-761], sepd. from oil, recrystallized from hot aq., m.p. 178° (5).

3:5640 (1) Lieben, *Ann.* **146**, 181–186 (1868). (2) Natterer, *Monatsh.* **5**, 496–497 (1881). (3) Mohler, Sorge, *Helv. Chim. Acta* **23**, 1209 (1940). (4) Wildman, Gray, *J. Am. Chem. Soc.* **41**, 1122–1123 (1919). (5) Hantzsch, Wild, *Ann.* **289**, 293 (1896). (6) Mohler, Hartnagel, *Helv. Chim. Acta* **25**, 859–863 (1942); *C.A.* **37**, 1709 (1943).

3:5650 1,2,3-TRICHLOROPROPENE-1

$C_3H_3Cl_3$ — Beil. I-200, I_1—, I_2—

$$ClCH_2—\overset{\text{Cl}}{C}=CHCl$$

B.P. 142° (1)

$D^{20}_{20} = 1.414$ (1)

Liq., insol. aq., eas. sol. alc., ether. [Two geom. stereoisomers are possible but unrecorded.]

[For prepn. of C̄ from 1,2,2,3-tetrachloropropane (3:5805) with alc. alk. see (1).]

[For use in prepn. of unsatd. cellulose ethers see (2); for use in dewaxing mineral oils see (3).]

3:5650 (1) Pfeffer, Fittig, *Ann.* **135**, 361–363 (1865). (2) du Pont Co., Brit. 429,040, June 11, 1935; *Cent.* **1936**, I 4098; *C.A.* **29**, 7073 (1935). (3) Standard Oil Development Co., French 790,852, Nov. 28, 1935; *Cent.* **1936**, I 2672; *C.A.* **30**, 3223 (1936).

3:5655 METHYL DICHLOROACETATE $C_3H_4O_2Cl_2$ $Cl_2CH.COOCH_3$ Beil. II - 203 II_1— II_2-(196)

B.P. 143.3°	at 764.5 mm.	(1)	$D_{19.2}^{19.2} = 1.3808$ (6)
143.2°		(2)	
143°		(3) (8)	
142–144°		(4)	
49.8–50°	at 20 mm.	(5)	

[For prepn. of C̄ from dichloroacetic acid (3.6208) with MeOH + HCl gas (72% yield (3)) (7), with MeOH + $Et_2O.BF_3$ complex (70% yield (3)), with MeOH + H_2SO_4 (71.3% yield (3)), or with MeOH itself without any cat. (47–61% yield (3)), or with Me_2SO_4 in s.t at 200° (8) see indic. refs.; for prepn. of C̄ from dichloroacetamide with BF_3 in MeOH (57% yield) see (3); for prepn. of C̄ from chloral (3:5210) (84% yield (9)), chloral hydrate (3:1270) (4), or chloral hydrate diacetate (76% yield (9)) with KCN in MeOH see indic. refs.]

[For reactn. of C̄ with dimethyl sodio-malonate in MeOH yielding (10) 1,1,2,3,3-penta-(carbomethoxy)propane [Beil. II-880], tbls. from MeOH + aq , m.p. 85–86° see (10).]

C̄ on hydrolysis yields dichloroacetic acid (3:6208) q.v. + MeOH (1:6120). [For studies of rate of hydrolysis under various circumstances see (5) (11)]

3:5655 (1) Schiff, *Z physik Chem* **1**, 378 (1887) (2) Cheng, *Z. physik. Chem.* **B-24**, 305 (1934). (3) Toole, Sowa, *J. Am Chem. Soc* **59**, 1971–1973 (1937). (4) Wallach, *Ann.* **173**, 299 (1874). (5) Skrabal, *Monatsh.* **71**, 298–308 (1938) (6) Henry, *Compt rend* **101**, 251 (1885). (7) Müller, *Ann.* **133**, 160 (1865). (8) Simon, *Compt rend.* **176**, 585 (1923). (9) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1042, 1047. (10) Anschütz, Deschauer, *Ann.* **347**, 6–7 (1906).
(11) Skrabal, Rückert, *Monatsh.* **50**, 369–384 (1928).

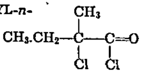
3:5660 1,1,3-TRICHLOROPROPANE $ClCH_2.CH_2.CHCl_2$ $C_3H_5Cl_3$ Beil. I - 106
(β-Chloropropylidene (di)-chloride) I_1— I_2—

B.P. 143–144° (1)	$D_-^{18} = 1.351$ (1)	$n_-^{18} = 1.474$ (1)
146–148° (2) (3)	$D_{15}^{15} = 1.362$ (3)	

C̄ with alc. KOH splits out HCl yielding (2) (3) 3,3-dichloropropene-1 (3:5140), b.p. 84°, together with a little 1,3-dichloropropene-1 (3.5280), b p. 107°.

3:5660 (1) Kirrmann, Pacaud, Dosque, *Bull soc. chim* (5) **1**, 866 (1934). (2) Gustavson, *J. prakt. Chem.* (2) **50**, 381–382 (1894). (3) van Romburgh, *Bull soc chim* (2) **37**, 100–102 (1882).

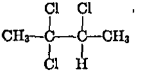
3:5670 *d,l*-α-CHLORO-α-METHYL-*n*-BUTYRYL CHLORIDE $C_5H_8OCl_2$ Beil. II -307 II_1— II_2—



B.P. 143–144° at 749 mm. (1) $D_-^{14} = 1.187$ (1)

[For prepn. of C̄ from α-chloro-α-methyl-*n*-butyric acid (3:8718) with PCl_3 see (1).]
C̄ on hydrolysis with aq. yields (1) α-chloro-α-methyl-*n*-butyric acid (3:8718) q.v.

3:5670 (1) Servais, *Rec trav chim.* **20**, 59 (1901).

3:5680 2,2,3-TRICHLOROBUTANE  $C_4H_7Cl_3$ **Beil. S.N. 10**

B.P. 143–145° (2)		D_4^{20} = **1.2699** (1)	n_D^{20} = **1.4645** (1)
141–143° (1)		D_4^{18} = **1.2630** (2)	n_C^{18} = **1.4637** (2)
77–84° at 15 mm. (2)		D_4^{12} = **1.33** (2)	n_C^{12} = **1.4975** (2)

[For prepn. of C̄ (45% yield (2)) from 2-chlorobutene-2 (3:7105) (together with 55% 2,3-dichlorobutene-1 (3:9074)) with Cl_2 + $NaHCO_3$ at 0° (2) (3) or with Cl_2 + $SnCl_4$ in dark (4) see indic. refs.; for formn. of C̄ (28% yield (1)) from 1,2-dichlorobutane (3:7680) + sl. excess Cl_2 in dark at −17° (together with 19% 1,2,3-trichlorobutane) (3:5935) see (1); for formn. of C̄ (18% yield (1)) from 2,3-dichlorobutane (3:7615) + sl. excess Cl_2 in dark at −17° (together with 36.5% 1,2,3-trichlorobutane (3:5935)) see (1).]

C̄ with solid KOH at 140° loses HCl yielding (1) mixt. of *cis*-2,3-dichlorobutene-2 (3:5500), and *trans* 2,3-dichlorobutene-2 (3:7395).

3:5680 (1) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1553–1558 (1936); *C.A.* **31**, 2165 (1937); *Cent.* **1937**, I 3786. (2) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **8**, 1232–1246 (1938); *C.A.* **33**, 4190 (1939); *Cent.* **1939**, II 4222. (3) du Pont Co., Brit 535,586, April 15, 1941; *C.A.* **36**, 1337 (1942). (4) Levine, Cass (to du Pont Co.) U.S. 2,323,227, June 29, 1943; *C.A.* **38**, 119 (1944).

3:5690 β-CHLOROPROPIONYL CHLORIDE $C_3H_4OCl_2$ **Beil. II - 250**
$ClCH_2.CH_2.CO.Cl$ **II_1—**
II_2-(227)

B.P. 144.5°		(1)	D_-^{13} = **1.3307** (3)
144°		(2)	
143–145°	at 763 mm.	(3)	
82–82.5° cor.	at 102 mm.	(4)	
87°	at 95 mm.	(5)	
53°	at 23 mm.	(5)	

Pale yel. liq. with pungent odor, sol. alc., ether, acetone, $CHCl_3$ (1).

[For prepn. from β-chloropropionic ac. (3:0460) with PCl_3 (3) or $SOCl_2$ (96% yield (5)) see (3) (2) (5); from propionyl chloride (3:7170) + Cl_2 see (4) (9); from phosgene (3:5000) + ethylene + $AlCl_3$ see (1) (this method questioned by (6) (7)).]

C̄ over Al_2O_3 at 250° loses 1 HCl giving (35% yield (10)) (11) acryloyl chloride (3:7153).

Ⓓ **β-Chloropropionic acid** (3:0460): lfts. from lgr. or pet. ether, m.p. 42°. [From C̄ on boilg. with aq. (1).]

Ⓓ **β-Chloropropionamide**: unrecorded.

Ⓓ **β-Chloropropionanilide**: cryst. from aq. or MeOH, m.p. 119° (8). [From C̄ + aniline in acetone; 90% yield (8).]

Ⓓ **β-Chloropropion-*p*-toluidide**: cryst. from MeOH, m.p. 121° (8) (2).

3:5690 (1) Paco, *Gazz. chim. ital.* **59**, 580–582 (1929). (2) Wolffenstein, Rolle, *Ber.* **41**, 736 (1908). (3) Henry, *Compt. rend* **100**, 115 (1885); *J. prakt. Chem.* (2) **31**, 127 (1885). (4) Michael, *Ber.* **34**, 4047–4048 (1901). (5) Fieser, Seligman, *J. Am. Chem. Soc.* **58**, 2484 (1936). (6) Frolich, Wiezevich, *Ind. Eng. Chem.* **24**, 16 (1932). (7) Varshavskii, Doroganyevskaya, *Gazz. chim. ital.* **64**, 53–59 (1934). (8) Mayer, van Zütphen, Philipps, *Ber.* **58**, 860 (1927); Mayer, Ger. 415,096, June 13, 1925; *Cent.* **1925**, II 1094. (9) Schmidt, Schloffer (to I.G.) Ger. 738,398 [illegible] *Soc.* **66**, 371 (1944). [illegible] (1936): Brit. 333,079, [illegible]

3:5700 ETHYL CHLOROACETATE $CH_2.COOC_2H_5$ (with Cl on CH_2) $C_4H_7O_2Cl$ Beil. II - 197 II_1-(88) II_2-(191)

B.P.			F.P.				
144.5–144.9°	at 754.2 mm.	(1)	−26° (13)	D_4^{20} = 1.1561 (11)		n_D^{20} = 1.42162	(8)
143.8–144.2°		(2)		1.1520 (8)		1.4205	(14)
143.7–144.2° cor.		(3)		1.1498 (14)		1.4203	(11)
143.6°	at 760 mm.	(4)					
143.5°	at 758 mm.	(5)		D_{20}^{20} = 1.1573 (3)			
143°	at 756 mm.	(6)					
142.8°		(7)					
142.6–143.0°	at 750 mm.	(8)					
142.0–142.3°	at 743 mm.	(9)					
141–142.5°	at 738 mm.	(10)					
140–142°	at 735 mm.	(11)					
52°	at 20 mm.	(12)					

Colorless liq.; for constant-boilg. mixt. of C̄ with various org cpds. see Beil. II_2-(191) or (4) (15) (16) —[For insecticidal actn. see (17); for use in refining of mineral oil see (18).]

[For prepn. of C̄ from chloroacetic acid (3:1370) with EtOH + dry HCl gas (10) cf. (72.5% yield (22)) or H_2SO_4 (70% yield (23)) (19) or anhydrous $MgCl_2$ (20) see indic. refs.; from chloroacetyl chloride (3:5235) with EtOH (5) or with triethyl orthoformate (1:3241) at 100–110° (90% yield (21)) see indic. refs.; from α,β-dichlorovinyl ethyl ether (3:5540) with org. acids see (24) (25).]

[For formn. of C̄ from ethyl hydroxyacetate (ethyl glycolate) with PCl_5 see (26); from ethyl aminoacetate hydrochloride with $NaNO_2$ + excess HCl see (27); from ethyl diazoacetate with HCl (27) (28) or with $HgCl_2$ (70% yield (11)) see indic. refs.; from dichloroacetaldehyde monoethyl hemiacetal (3:5310) with alc. KCN at 20° (38% yield) see (29); from ethyl α-chloroacetoacetate (3:6207) with diethyl sodiomalonate see (30).]

C̄ refluxed with KF yields KCl + ethyl hydroxyacetate (+ some ethyl fluoroacetate) (31); C̄ with MgI_2 in ether (32) or KI in alc. (3) (34) or in acetone at ord. temp. (35) yields ethyl iodoacetate, b.p. 180°. [For studies on rate of reactn. of C̄ with KI in acetone see (36) (37) (38); with NaI or LiI in acetone see (38).]

[*C̄ with Al/Hg + a trace of alc. (39) or with Mg + trace of I_2 in ether (40) or C̄ with* Mg + trace $HgCl_2$ in ether (41) yields ethyl γ-chloroacetoacetate (3:6375), b.p. 205°; C̄ with NaCN (25) or KCN (42) yields ethyl cyanoacetate, C̄ with ethyl sodioacetoacetate gives (56–62% yield (23)) diethyl acetosuccinate.]

[C̄ with 2 moles MeMgBr (but not MeMgI) in ether gives (yield: 60% (43), 38% (44)) 1-chloro-2-methylpropanol-2 (3:7752) (note, however, that C̄ with a large excess MeMgBr (4 moles) gives (40% yield (45)) 2-methylbutanol-3 (1:6170) (3,5-dinitrobenzoate, m.p. 74–75°)); for reactn. of C̄ with EtMgBr yielding (46) 3-(chloromethyl)-pentanol-3 [Beil. I-412], with isopropyl MgCl (47), or with phenyl MgBr (3 moles) yielding (48) chloromethyl-diphenyl-carbinol [Beil. VI-685] see indic. refs.]

[For use of C̄ with Zn (or Zn + Cu (49)) + ketones to give by Reformatsky reactn. (50) β-hydroxy-esters see indic. refs.]

C̄ treated with aq. benzenediazonium chloride + NaOAc gives (15% yield (6)) ethyl γ-chloro-β-phenylhydrazono-acetoacetate, m.p. 92–93° (6).

C̄ with Me_3N in abs. alc. followed by treatment with 100% hydrazine hydrate as directed (51) (52) gives 83–89% yield (51) betaine hydrazide hydrochloride, $(CH_3)_3N(Cl).CH_2$-

CO.NH.NH_2 (Girard's reagent for ketones), m.p. 192°. [For corresp. reactn. using pyridine instead of Me_3N see (52).]

$\bar{C}$ shaken in cold with 2 vols. conc. aq. NH_4OH gives (53) (54) (28) (29) (78-84% yield (55)) chloroacetamide, cryst. from aq., m.p. 119-120° (55), 120° (28). — $\bar{C}$ htd. at 100° for ½ hr. with 2 moles aniline, cooled, aniline hydrochloride extracted with aq. gives (100% yield (56)) (57) (58) ethyl anilinoacetate (phenylglycine ethyl ester) [Beil. XII-470, XII_1-(203)], cryst. from dil. alc. (56) (57) or lgr. (58), m.p. 58° (58), 57-58° (57), 57° (56). [This prod. on boilg. with excess aniline yields (57) anilinoacetanilide (phenylglycine anilide) [Beil. XII-556], m.p. 110-111° (57).] — $\bar{C}$ htd. with aq. benzylamine yields (59) chloroacet-N-benzylamide, m.p. 93.0-93.C° cor. (59).

[$\bar{C}$ with ethyl carbamate ("urethane") + Na in dry ether as directed gives (51-57% yield (60)) triethyl N-tricarboxylate = $N(COOC_2H_5)_3$ [Beil. III-28], b.p. 146-147° at 12 mm. (60).]

$\bar{C}$ htd. as directed (60) with K tetrachlorophthalimide yields N-(carbethoxymethyl)-tetrachlorophthalimide, ndls. from $CHCl_3$ on pouring into 2 vols. MeOH, m.p. 180-181° (60); $\bar{C}$ with Na phthalimide yields (61) N-(carbethoxymethyl)phthalimide, m.p. 112-113° (61); $\bar{C}$ with K 3-nitrophthalimide yields (62) N-(carbethoxymethyl)-3-nitrophthalimide, ndls. from alc., m.p. 79-80° (62).

$\bar{C}$ on hydrolysis (e.g., by boilg. 10 min. with $N/10$ aq. $Ba(OH)_2$ (14)) yields ethyl alcohol (1:6130) and chloroacetic acid (3:1370). [For studies on the kinetics of hydrolysis of $\bar{C}$ under various conditions see Beil. II_2-(191-192) and (2) (14) (63) (64) (65).]

(54) Tröger, Hille, *J. prakt. Chem.* (2) **71**, 204 Note (1905). (55) Jacobs, Heidelberger, *Org. Syntheses*, Coll. Vol. **1** (2nd ed.), 153–154 (1941); (1st ed.), 147–148 (1932); **7**, 16–17 (1927). (56) Gault, *Bull soc. chim.* (4) **3**, 370 (1908). (57) Meyer, *Ber.* **8**, 1156–1158 (1875). (58) Bischoff, Hausdorfer, *Ber.* **25**, 2270 (1892). (59) Buehler, Mackenzie, *J. Am. Chem. Soc.* **59**, 421–422 (1937). (60) Allen, Nicholls, *J. Am. Chem. Soc.* **56**, 1409–1410 (1934).

(61) Weisz, Lanyi, *Magyar Chem. Folyoirat*, **39**, 153–155 (1933); *Cent.* **1934**, I 2746, *C.A.* **28**, 5815 (1934). (62) Sah, Ma, *Ber* **65**, 1630–1633 (1932). (63) Sapazhinikova, *J. Phys. Chem. (U.S.S.R.)* **13**, 174–185 (1939), *C.A.* **34**, 311 (1940). (64) Anantakrishnan, Krishnamurti, *Proc. Indian Acad Sci.* **14-A**, 270–278, 279–288 (1941), *C A* **36**, 1837 (1942). (65) Newling, Hinshelwood, *J. Chem. Soc.* **1936**, 1357–1361. (66) Allen, Bell, *Org. Syntheses*, **24**, 60–61 (1944).

3:5710 1,1,2-TRICHLORO-2-METHYLPROPANE

CH_3—C(CH_3)(Cl)—$CHCl_2$ $C_4H_7Cl_3$ Beil. I - 126, I_1—, I_2—

B.P.			M.P.	
144.5–145.4° cor.		(1)	**−6.5 to −6.0°** (1)	D_4^{25} = **1.2712** (1)
145–146°	at 762 mm.	(2)		n_D^{20} = **1.4666** (1)
46–47°	at 18 mm.	(2)		

[For prepn. (together with other products) from *ter*-butyl chloride (3:7045) + Cl_2 see (1), for formn. (32%) (together with 68% 3,3-dichloro-2-methylpropene-1) from 1-chloro-2-methylpropene-1 (3:7120) with Cl_2 + $NaHCO_3$ at 0° see (2).] [The product described in Beil. I-126 was very impure (1).]

C̄ on further chlorination yields (1) 1,1,1,2-tetrachloro-2-methylpropane (3:4725), m.p. 179°.

C̄ on prolonged refluxing with dil. NaOH loses ⅓ of its chlorine (1) but the reactn. products were not characterized.

3:5710 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1027–1029 (1936). (2) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* **8**, 1232–1246 (1938), *C.A.* **33**, 4190 (1939); *Cent.* **1939**, II 4222.

3:5725 1,4-DICHLOROBUTENE-2

ClH_2C—CH=CH—CH_2Cl $C_4H_6Cl_2$ Beil. S.N. 12

B.P.		
145° (1)		$n_D^{30.5}$ = **1.4745** (1)
75–76° at 40 mm. (1)		

For this structure two geom. stereoisomers are theoretically possible but only C̄ (configuration undetermined) is known.

[For prepn. of C̄ together with other products) from butadiene-1,3 with Cl_2, either directly or in $CHCl_3$, CS_2, or lgr. soln. see (1) (2); the process can be controlled so as to yield little or no 1,2,3,4-tetrachlorobutane but rather a mixt. of C̄ and 1,2-dichlorobutene-3 (3:5350) in the ratio 1:2 (1) (2): for prepn. of C̄ from 1,2-dichlorobutene-3 (3:5350) via allylic transposition in pres. of metal halide cat (3) such as $AlCl_3$ (4) see (3) (4).]

C̄ does *not* (1) rearr. to 1,2-dichlorobutene-3 (3:5350) even on htg. at 90° in a s t.

C̄ on htg. at 90° with 2 pts. solid KOH loses HCl yielding (1) 1-chlorobutadiene-1,3 (3:7210), b.p. 85° (1).

C̄ on htg. in alc. with Zn dust yields (1) butadiene-1,3.

C̄ with Cl_2 yields mainly (1) the *solid* form (m.p. 72°) of 1,2,3,4-tetrachlorobutane (3:1760).

C̄ on oxidn. with dil. alc. $KMnO_4$ or with O_3 followed by aq. gives (1) chloroacetic acid (3:1370).

3:5725 (1) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4043–4055 (1930). (2) Muskat (to du
(3) I. G. Farben-
(1939); Nicodemus,
icodemus (to I.G.),

3:5735 β-CHLOROETHYL ACETATE

$C_4H_7O_2Cl$ Beil. II - 128

$Cl.CH_2.CH_2.O.CO.CH_3$ II_1-(57)

II_2-(130)

B.P. 145° (1)
142–144° at 743 mm. (2)
142.4–143.8° at 733 mm. (3)

D_{27}^{27} = **1.1455** (2) n_D^{20} = **1.4234** (2) (3)

Colorless oil, insol. aq.

[For prepn. from β-chloroethanol (3:5552) by actn. of AcCl (90% yield (4), 82% yield (5)) see (4) (5) (6); by actn. of Ac_2O at 110° see (7); for prepn. from ethylene oxide (1:6105) + AcCl see (3) (8); for prepn. from ethylene glycol diacetate (1:3511) + HCl + ht. + pressure see (9); for prepn. from ethylene + Cl_2 + Ac_2O see (2) (10); for prepn. (95.5% yield (11)) from di-(β-chloroethyl) sulfate + NaOAc + AcOH see (11); for still other misc. methods see Beil. II-128.]

[For study of reactivity toward KI in acetone at 50° and 60° see (12); for study of pyrolysis (to vinyl chloride) see (13); for conversion to ethylene oxide (1:6105) by treatment with alk. see (14) (15).]

C̄ htd. at 100° for 5 hrs. with thiourea (1 mole) gives 100% yield of *S*-(β-acetoxyethyl)-isothiourea hydrochloride, cryst. from mixt. of alc. + acetone, m.p. 136–137° (17).

C̄ on hydrolysis yields β-chloroethanol (3:5552) + AcOH. [For study of hydrolysis by *N*/10 HCl see (16).]

Ⓓ ***N*-(β-Acetoxyethyl)tetrachlorophthalimide:** pl. from $CHCl_3$ poured into 2 vols. MeOH, m.p. 168–169° (18). [From C̄ + K tetrachlorophthalimide (18).]

3:5735 (1) Simpson, *Ann.* **112**, 149 (1859). (2) Baum, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1458 (1939). (3) Gustus, Stevens, *J. Am. Chem. Soc.* **55**, 383 (1933). (4) Bogert, Slocum, *J. Am. Chem. Soc.* **46**, 766 (1924). (5) Blicke, Blake, *J. Am. Chem. Soc.* **53**, 1018 (1931). (6)
(8) Altwegg, Landrivon,
man (to Dow Chem. Co.),
720, Feb. 3, 1937; *C.A.* **31**,
4073 (1937).

(11) Suter, Evans, *J. Am. Chem. Soc.* **60**, 537 (1938). (12) Conant, Kirner, Hussey, *J. Am. Chem. Soc.* **47**, 498 (1925). (13) Bilger, Hibbert, *J. Am. Chem. Soc.* **58**, 825 (1936). (14) Britton, Coleman, Mate (to Dow Chem. Co.), U.S. 2,022,182, Nov. 26, 1935; *C.A.* **30**, 737 (1936); *Cent.* **1936**, 113 11
371–2
(18)

3:5745 2,2-DICHLOROETHANOL-1
(β,β-Dichloroethyl alcohol)

$C_2H_4OCl_2$ Beil. I - 338

I_1—

I_2—

$$\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{HC}}\text{—}CH_2OH$$

B.P. 140° (1)
140–145° (2)

D_{19}^{19} = **1.416** (2) $n_D^{17.3}$ = **1.4752** (2)

Colorless liq.; sparingly sol. aq., sol. alc. or ether; volatile with steam.

[For prepn. of C̄ from β,β-dichloroacetaldehyde (3:5180) with $Al(OEt)_3$ in abs. alc. (2) or with diethylzinc followed by aq. (1) see indic. refs.]

C̄ reduces $NH_4OH/AgNO_3$ (1) (2).

C̄ on oxidn. with HNO_3 yields (1) dichloroacetic acid (3:6208).

3:5745 (1) Delacre, *Jahresber.* 1887, 1247. (2) Boeseken, Tellegen, Plusje, *Rec. trav. chim.* 57, 75–76 (1938)

3:5750 1,1,2,2-TETRACHLOROETHANE $Cl_2CH—CHCl_2$ $C_2H_2Cl_4$ Beil. I - 86
(Acetylene tetrachloride; I_1-(25)
sym.-tetrachloroethane) I_2-(55)

B.P.	F.P.		
147° cor. (1)	−44° (17)	D_4^{25} = 1.5881 (12)	
146.2–146.8° at 760 mm. (2)	−43.8° (4) (5)	1.5869 (19) (20)	
146.35° (3)	−43.5° (18)	1.58658 (5)	
146.3° at 758 mm. (17)	−42.5° (6) (18)		n_D^{24} = 1.501 (21)
146.25° (4)			
146.2–146.7° cor. at 756 mm. (20)		D_4^{20} = 1.5966 (2)	n_D^{20} = 1.49509 (22)
		1.59457 (5)	1.4947 (13)
146.20° at 760 mm. (5) (6)		1.5943 (9)	1.49419 (8)
145.6° (7)			1.49415 (2)
145.2° at 748 mm. (8)			1.4940 (9)
145.2° at 737 mm. (9)			
145–146° at 753 mm. (10)			$n_D^{18.5}$ = 1.49490 (23)
145.0° (11)			
144.7° at 751 mm. (12)			n_D^{17} = 1.49559 (24)
144.5° (13)			
144.0–144.8° (14)		D_4^{15} = 1.60255 (5)	n_D^{15} = 1.49678 (5)
143.5–144° (15)		1.6015 (12)	
140.6° at 675 mm. (12)			
136.0° at 594 mm. (12)		For D_4^t from −21° to 128° see (17).	For n_α^t from 13–25° see (11).
130.0° at 502 mm (12)			
125.3° at 435 mm. (12)			
120.5° at 372 mm. (12)			
115.0° at 313 mm. (12)			
108.0° at 252 mm. (12)			
102.0° at 203 mm. (12)			
90.0° at 132 mm. (12)			
80.0° at 89 mm. (12)			
62.0° at 45 mm. (12)			
55.5–56.3° at 31 mm. (16)			
55° at 17 mm. (12)			

Note: Care must be taken not to confuse C̄ with tetrachloroethylene (3:5460) or with 1,1,1,2-tetrachloroethane (*unsym.*-acetylene tetrachloride (3:5555)).

Colorless liq. with odor similar to that of chloroform. — [For vapor press. of C̄ at intervals over range 20–145° see (25); for study of thermal conductivity see (26).]

C̄ is very spar. sol. aq.: e.g., 100 g. H_2O at 20° dis. 0.288 g. C̄; at 55–56° dis. 0.336 g. C̄ (27); 1 g. C̄ is sol. at 25° in 350 g. aq. (101); for soly. of H_2O in C̄ at 0°, 25°, and 30° as

detd. by Karl Fischer reagt. see (28). — C̄ is easily volatile with steam (for use in detn. of H_2O see below).

MISCELLANEOUS PHYSICAL PROPERTIES

[For soly. in C̄ of dry gaseous HCl (14) (15), H_2S (14), or O_2 (29) see indic. refs.; for soly. in C̄ at 11–25° of I_2 (30) and use of such solns. in detn. of iodine number (31) see indic. refs.; for adsorption by activated carbon of I_2 from solns. in C̄ see (32).]

[For study of influence of vapors of C̄ on the explosion limits of mixtures of air with hydrogen (33), acetylene (33), methane (33) (34) (35), or carbon monoxide (33) (36) see indic. refs.]

[For prepn. of and comparison with C̄ of *sym.*-dideuteroiotetrachloroethane, $Cl_2C(D)$.-$C(D)Cl_2$, see (9).]

Binary systems contg. C̄. [For f.p./compn. data and/or diagrams on systems C̄ + 1,2-dichloroethane (ethylene dichloride) (3:5130) (18); C̄ + 1,1,2-trichloroethane (3:5330) (18); C̄ + pentachloroethane (3:5880), eutectic, f.p. −73°, contg. 40.1% C̄ (18); C̄ + *cis*-dichloroethylene (3:5042) (37); C̄ + *trans*-dichloroethylene (3:5028) (37); C̄ + *p*-dichlorobenzene (3:0980) (38); C̄ + 1,2-dibromoethane (ethylene dibromide) (18); C̄ + 1,1,2,2-tetrabromoethane (acetylene tetrabromide) (18); C̄ + succinonitrile (18); or C̄ + succinic acid (1:0530) (18) see indic. refs. — For study of system C̄ + naphthalene (1:7200) at 30° under press. up to 1000 atm. see (39).]

C̄ with various org. cpds. forms binary azeotropes [e.g., C̄ with anhydrous formic acid (1:1005) forms a const.-boilg. mixt., b.p. 99.25° at 760 mm., contg. 32 wt. % C̄ (40): note that C̄ with AcOH (1:1010) does *not* form a const.-boilg. mixt. (41) (the data listed by "Int. Crit. Tables" for such an azeotrope is actually for the mixt. AcOH + tetrachloroethylene); C̄ with propionic acid (1:1025) forms a const.-boilg. mixt., b.p. 140.4° at 760 mm., contg. abt. 40 wt. % C̄ (12); for other azeotropes see Beil. II_2-(56). — Note that no record of formn. of azeotropes of C̄ with MeOH or EtOH can be found.]

Ternary systems contg. C̄. [For soly. data and diagrams of system C̄ + acetone (1:5400) + aq. see (43).]

USES OF C̄

C̄ is widely used in industry as a solvent and as an intermediate in the manufacture of various other chlorinated solvents, notably trichloroethylene (3:5170); for additional examples of special uses see also below.

C̄ is frequently employed as solvent in certain types of Friedel-Crafts reactions or phthalic anhydride condensations [for study of use of C̄ as solvent in Friedel-Crafts condensation of phenol with high-mol.-wt. acyl chlorides see (44)].

[For use of C̄ as swelling agent for rubber (45), in prod. of films from rubber hydrochloride (46), in prod. of cellulose acetate by pptn. from C̄ with hydrocarbons (47) (note that acetylcelluloses give with C̄ crystalline addition prods. (48)), together with aliphatic monohydric alcs. as solv. for cellulose alkyl ethers (49), in prepn. of transparent cellulose acetate plastics (50) see indic. refs. — For soly. of various polymers in C̄ see (56).]

[For use of C̄ as catalyst in condensation of phenol with formaldehyde (51) or furfural (52) see indic. refs.]

[For use of C̄ with petroleum naphtha as a dry-cleaning fluid (53), for use of C̄ as a rust remover (54), as means of removing mud barriers in oil wells (55), or as an immersion fluid in opt. crystallog. (21) see indic. refs.]

[For use of C̄ (57) (58) or stable aq. emulsions of C̄ (59) as weed killers see indic. refs.]

[For studies of use of C̄ in detn. of theobromine in cacao see (60) (61) (62) (63).]

[For use of C̄ as anti-moth prod. (64), as a component of insecticides (65), together with

CS_2 and chlorobenzene (3:7903) as insecticide (66), or together with 20% trichloroethylene (3:5170) as a fumigant and insecticide (67) see indic. refs.]

[For studies on antiseptic, bactericidal, and disinfectant action of $\bar{C}$ see (68) (69) (70).]

$\bar{C}$ is also employed for the detn. of H_2O by distillation; note that besides being non-inflammable $\bar{C}$ is also much denser than water which for some applications of this method is advantageous. — [For general discussion and examples of this procedure see (226) (70) (71) (72) (73) (74) (75); for comparison of results with those obtd. by oven drying see (76); for application to detn. of H_2O in liquid and solid fuels (77) (78), in glycerol (79) (80), in liquid glue (81), in cereal (82), in dried apples (83), in cooking salt (84) see indic. refs.]

TOXICITY AND PHYSIOLOGICAL ACTION OF $\bar{C}$

$\bar{C}$ is the most toxic of the group of chlorinated hydrocarbons (85) and produces marked pathological alterations in gastrointestinal tract, liver, and kidneys. — [Detailed discussion of this aspect of $\bar{C}$ is beyond the scope of this treatment except to cite references (229) (227) (232) and (85)–(99), incl. (note that articles on this topic prior to 1930 are omitted).]

[For discussion of fate of $\bar{C}$ in body see (100). — Note also that $\bar{C}$ (in sharp contrast to the closely related tetrachloroethylene (3:5460)) has no efficacy as anthelmintic for hookworms (101).]

[For actn. of $\bar{C}$ on alc. fermentation see (102) (103); for actn. on invertase see (104).]

DETERMINATION OF $\bar{C}$

Some methods for the detn. of $\bar{C}$ involve conversion of all of its halogen to chloride ion and subsequent volumetric or gravimetric detn. of the latter; e.g., for methods based on initial pyrolytic decomposition see (105) (89) (106) (107); for methods based on dehalogenation of $\bar{C}$ with Na + ethanolamine in dioxane see (108) (230) (note that use of Na in liq. NH_3 causes some cyanide formn. (109)). — For detn. of $\bar{C}$ by means of elimination of 1 HCl with cold alc. KOH see (110). — For detn. of $\bar{C}$ by means of the Fujiwara color reactn. with NaOH/pyridine see (111). — Note that $\bar{C}$ does not respond to the R + H "Tri-Per-Analyzer" (a recording ultra-violet photometer) (112). — For further comments on detection of $\bar{C}$ see below under color tests.

PREPARATION OF $\bar{C}$

$\bar{C}$ is one of a large family of "chlorinated solvents" now available from industrial sources. — The most-studied method of prepn. is that from acetylene by controlled addition of chlorine, although variants of this method are employed and other starting prods. (see below) are sometimes used. — $\bar{C}$ is also obtained as a by-prod. of the manufacture of the comml. mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes, *cis* (3:5042) and *trans* (3:5028), 1,1,2-trichloroethane (3:5330), etc.

From acetylene by addition of chlorine. Under suitable controls to avoid explosion and with the assistance of a wide variety of catalysts $\bar{C}$ is manufactured from acetylene by reaction with Cl_2. — [For a concise review of the general nature and difficulties of this general method see (113).]

[For important general articles on this synthesis see (114)–(122) incl. — For examples of patents employing this method see refs. (123)–(138) incl.; for special test of Ger. 204,833 (131) see (118) (120); for test of Ger. 154,677 (133) see (119) (120).]

From acetylene by other means. [For prepn. of $\bar{C}$ from acetylene with excess $SbCl_5$ (139) (234) with $SbCl_3 + SbCl_5$ (140), with NOCl (4 moles) at 350° (141), with aq. NaOCl soln. (142), with S_2Cl_2 + Fe powder in cold (143) (144) see indic. refs.]

From ethylene. [For formn. of $\bar{C}$ from ethylene + Cl_2 (as by-prod. of prepn. of ethylene chlorohydrin (3:5552)) (145), from ethylene + Cl_2 (as by-product of prepn. of 1,1,2-trichloroethane (3:5330)) (146) (147), from ethylene + Cl_2 (as by-prod. of a three-part process for combined prepn. of $\bar{C}$ + ethyl chloride) (198) see indic. refs.

From dichloroethylenes. [For prepn. of $\bar{C}$ from *cis*-dichloroethylene (3:5042) in vapor phase at 95° in light of 4360 Å with Cl_2 (in absence of O_2) (149), or in liq. phase with SO_2Cl_2 (1½ moles) in pres. of trace of dibenzoyl peroxide refluxed 3 hrs. in dark (85% yield (150)), see indic. refs.]

[For prepn. of $\bar{C}$ from *trans*-dichloroethylene (3:5028) in vapor phase at 80–95° in light of 4358 Å with Cl_2 see (151).]

[For prepn. of $\bar{C}$ from ord. mixt. (3:5030) of both stereoisomeric dichloroethylenes with Cl_2 (13) in light of 4360 Å (152) see indic. refs.]

From trichloroethylene. [For formn. of $\bar{C}$ (together with other prods.) from trichloroethylene (3:5170) + $AlCl_3$ + HCl gas at 50° see (153).]

From 1,2-dichloroethane (ethylene (di)chloride). [For prepn. of $\bar{C}$ from ethylene (di)chloride (3:5130) with Cl_2 (148) in u.v. light see (154).]

From miscellaneous starting points. [For formn. of $\bar{C}$ usually together with other prods. from dichloroacetaldehyde (3:5180) with PCl_5 (1), from "β-chlorovinyl iodochloride" ($ClCH{=}CH.ICl_2$) on warming (16), from 1,1,2-trichloro-2-iodoethane on distn. at ord. press. (155), from 1,2-di-iodoethylene with Cl_2 (156), or from 1,1,2-trichloroethane (3:5330) with Cl_2 + $AlCl_3$ at 70–80° (231) see indic. refs.]

STABILIZATION OF $\bar{C}$

[For patents on stabilization of $\bar{C}$ by addition of small amts. of phenols, aminophenols, etc. (157), or by addn. of less than 0.1% alkylamines (158) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis without catalyst. $\bar{C}$ on protracted reflux (20 days (159)) or techn. $\bar{C}$ on repeated distn. (160) leaves a residual high-boilg. fraction ("Tetranachlauf") consisting mainly of 1,1,2,3,4,4-hexachlorobutane (3:3155), ndls. from alc., m.p. 107° (159) (160), presumably formed by elimination of 1 Cl atom from each of 2 moles of $\bar{C}$. — [$\bar{C}$ htd. in s.t. at 300° for 15 hrs. yields (139) trichloroethylene (3:5170); $\bar{C}$ in s.t. at 360° for 100 hrs. yields (139) hexachlorobenzene (3:4939).]

Pyrolysis in pres. of various catalysts or HCl acceptors. $\bar{C}$ on suitable htg. particularly in the pres. of dehydrohalogenating catalysts or acceptors of the hydrogen chloride formed loses 1 mole HCl yielding trichloroethylene (3:5170). (For elimination of HCl by chemical means such as alk., NH_3, etc., see below.)

[E.g., $\bar{C}$ over pumice at 700° (161), over pumice contg. $Cu_2(PO_4)_3$ at 450–500° (162), over ThO_2 below 390° (163) cf. (164), over $BaCl_2$ at 300° (165), over bone char at 300–310° (166), over activated carbon at 200–300° (167), 260° (168) (note yield diminishes with increasing temp. (233)) or 500° (169), or over suitable cat. (148) loses HCl yielding trichloroethylene (3:5170). — Note also that pure $\bar{C}$ on long exposure to u.v. light loses HCl bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.]

[$\bar{C}$ + acetylene over cat. at 250° loses HCl yielding (167) trichloroethylene (3:5170) + vinyl chloride (3:7010); $\bar{C}$ with MeOH over Al_2O_3 at 280° loses HCl yielding (170) trichloroethylene (3:5170) + methyl chloride (3:7005).]

Dehydrogenation. [$\bar{C}$ with air over pumice contg. $CuCl_2$ at 430–450° (171), or with Cl_2 over activated carbon contg. $CuCl_2$ at 300–320° (172), or with hexachloroethane (3:4835) over cat. at 200–400° (173) loses its two hydrogenations yielding tetrachloroethylene (3:5460).]

(Partial) dehalogenation. [$\bar{C}$ with H_2 over Ni at 300–320° (174), or $\bar{C}$ with Fe or Al + aq. (175) (176) or Zn + aq. (176) (177), or $\bar{C}$ with acetylene over hydrogenating cat. (such as Ni) on activated carbon at 350° (178) preferably in pres. of aq. vapor (179) or on electrolytic reductn. in pres. of $ZnCl_2$ (235) (236) loses 1 chlorine from each carbon atom yielding a mixt. (3:5030) of the two stereoisomeric 1,2-dichloroethylenes. — Note that $\bar{C}$ with Zn in alc. yields (180) acetylene.]

Oxidation. [$\bar{C}$ with air in ultra-violet light yields (181) (182) dichloroacetyl chloride (3:5290) (or in pres. of aq. dichloroacetic acid (3:6208)), accompanied by small amts. of oxalic acid and an octachlorobutane, m.p. 81°. (Note also that pure $\bar{C}$ on long exposure to u.v. light loses HCl bimolecularly yielding (159) 1,1,2,3,4,4-hexachlorobutene-2 (3:1945), m.p. 80°.)]

[For behavior of $\bar{C}$ with CrO_3/H_2SO_4 (183) or over hot CuO (184) see indic. refs.]

Behavior with Halogens

Fluorination. [$\bar{C}$ with F_2 gas at 50° for 14 hrs. gives (185) 1-fluoro-1,1,2,2-tetrachloroethane, b.p. 115.5–116.5°, $D_4^{20} = 1.6218$, $n_D^{20} = 1.4487$, and 1,2-difluoro-1,1,2,2-tetrachloroethane, b.p. 92–93°, m.p. 24–25°, together with various other prods. — For fluorination of $\bar{C}$ with $SbF_3 + SbCl_5$ see (186)).]

Chlorination. [$\bar{C}$ with Cl_2 (139) in CCl_4 soln. (187), in u.v. light (188) or X-radiation (189), or over activated carbon at 300–400° (190) (191), or in liq. phase at 60–70° (192), or with Fe at 20–80° (192), or with $AlCl_3$ at 20–100° (192), or under reflux at 120° (80% yield (193)), or $\bar{C}$ with anhydr. $FeCl_3$ on htg. in s.t. (194), or even $\bar{C}$ with aq. bleaching powder (192) yields hexachloroethane (3:4835).]

Behavior with H_2SO_4

$\bar{C}$ with fumg. H_2SO_4 (65% SO_3) in pres. of $HgSO_4$ at 50–60° readily gives (198) (yields: 70–73% (195), 32% (196), 30% (197)) glyoxal sulfate, $O_2SO_2CH—CHO_2SO_2$, [Beil. I_2-(818)], ndls. from $ClSO_3H$, m.p. 176–177° (198), ndls. with 1 AcOH, m.p. 121–122° from AcOH, the solv. of crystn. being lost completely in vac. over NaOH (199).

Behavior with Alkaline Reactants

$\bar{C}$ under influence of many alk. reactants loses 1 mole HCl; this reactn. is used for the manufacture of trichloroethylene (3:5170) (see also above under pyrolysis of $\bar{C}$) and also by titration of the HCl or estimation of chloride ion formed as a diagnostic test for $\bar{C}$ (see below)

$\bar{C}$ on htg. with aq. alk. or alk. carbonates (200) in pres. of tetraethylene glycol as promoter (228) or with aq. $Ca(OH)_2$ or alk. carbonates (200) (201) (234) (114) (for test of Ger. 171,900 (200) see (202) (120)), or $\bar{C}$ with alc. KOH (203) cf. (122) or alc. NaOEt (203), loses 1 mole HCl yielding trichloroethylene (3:5170); note that in use of alc. alkali, distn. gives the const.-boilg. mixt. of EtOH with trichloroethylene, b.p. 70–71°, from which latter is separated by washing with aq. and subsequent drying over $CaCl_2$ (203).

$\bar{C}$ with EtOH/NaOH or EtOH/NaOEt (204) cf. (205), or $\bar{C}$ with 1 *N* EtOH/KOH in xylene (110), instantly and quant. splits out 1 HCl at room temp.; note that this does not occur with *cis*-dichloroethylene (3:5042), *trans*-dichloroethylene (3:5028), trichloroethylene (3:5170) or tetrachloroethylene (3:5460), chloroform (3:5050), or carbon tetrachloride (3:5100), but does occur in analogous fashion with pentachloroethane (3:5880) (110). — [For rate of reactn. of $\bar{C}$ with KOH in 95% EtOH at 90° see (206).]

Note, however, that $\bar{C}$ in acetone with *excess* standard alk. refluxed 3 hrs., then residual alk. titrated back, uses 5 equivalents of alk. (207); this surprising result is presumably to

be attributed to hydrolysis of $\bar{C}$ to glyoxal followed by disproportionation of latter to sodium glycolate; cf. (208).

$\bar{C}$ with solid KOH on htg. yields (203) dichloroethylene (3:5030), trichloroethylene (3:5170), tetrachloroethylene (3:5460), together with a spontaneously inflammable gas which may be chloroacetylene (3:7000). — $\bar{C}$ with anhyd. KOH in xylene at 80° under N_2 gives (209) a little dichloroacetylene (3:5010) (may be carried out as a lecture experiment (209)).

Behavior of $\bar{C}$ with NH_3 and Amines

[$\bar{C}$ with excess NH_3 gas in pres. of aq. (210), or with aq. NH_4OH htd. under press. (210) (120), or with liq. NH_3 at −40° (211) (212), or with dry pyridine on reflux (182) loses HCl giving (yields: 92% (211) 92–96% (210)) trichloroethylene (3:5170).]

[$\bar{C}$ htd. with aniline + aq. $Ca(OH)_2$ at 140–190° under press. yields (213) a mixt. of the calcium salt of *N*-phenylglycine and *N*-phenylglycine anilide, cf. (122); since this reaction really involves conversion of $\bar{C}$ by loss of HCl to 1,1,2-trichloroethylene (3:5170) and reactn. of latter with aniline see 3:5170 for details.]

$\bar{C}$ with excess phenylhydrazine on stdg. at ord. temp. evolves N_2, ppts. phenylhydrazine hydrochloride, and yields C_6H_6 (110); the full mechanism of this behavior seems never to have been established, but the same three prods. are also similarly obtd. from pentachloroethane (3:5880) and hexachloroethane (3.4835).

[For rate of reactn. of $\bar{C}$ with piperidine in 95% EtOH at 90° see (206).]

Behavior of $\bar{C}$ with Metals

[For survey of action of $\bar{C}$ on various common metals (214) (215) in pres. of moisture (223) see indic. refs.]

$\bar{C}$ with Na or K or their alloys may (like many other polychloro compounds) explode under certain conditions [for extensive studies of this behavior including sensitivity to mechanical shock see (216) (217)].

Behavior of $\bar{C}$ with Metal Salts

[$\bar{C}$ with $AlCl_3$ at 110° undergoes partial rearr. (218) to the isomeric 1,1,1,2-tetrachloroethane (3:5555). — $\bar{C}$ with freshly prepared anhyd. $AlBr_3$ on htg. below b.p. of $\bar{C}$ yields (219) 1,1,2,2-tetrabromoethane (acetylene tetrabromide) [Beil. I-94, I_1-(30), I_2-(66)].]

$\bar{C}$ with $N/15$ $AgNO_3$ in 95% EtOH shows no reactn. even after 12 hrs. at 90° (206) cf. (80).

MISCELLANEOUS

[$\bar{C}$ does *not* react with excess Hg di-*p*-tolyl (220). — $\bar{C}$ with excess C_6H_5MgBr yields 1,1,2,2-tetraphenylethane [Beil. V-739, V_1-(371), V_2-(673)] (221) cf. (222).]

COLOR REACTIONS OF $\bar{C}$

Ⓟ With cyclopentanol (1:6412). $\bar{C}$ (1 drop) with cyclopentanol (2 ml.) + trace solid NaOH, boiled 25 secs., cooled, acidified with AcOH or 85% H_2SO_4, stood 1 min., shaken gives (224) green color. [Note that this same response is also shown by 1,1,2-trichloroethylene (3:5170) but not by methylene dichloride (3:5020), $CHCl_3$ (3:5050), CCl_4 (3:5100), ethylene dichloride (3:5130), pentachloroethane (3:5880), *cis*-(3:5042) or *trans*- (3:5028) 1,2-dichloroethylene, or tetrachloroethylene (3:5460); for sensitivity for $\bar{C}$ see (224).]

With pyridine + NaOH (Fujiwara reagt.) [For detn. of $\bar{C}$ with Fujiwara reagt. see (111); for relative sensitivity of Fujiwara reagt. to $\bar{C}$ as compared to $CHCl_3$ (3:5050),

CCl_4 (3:5100), 1,1,2-trichloroethane (3:5330), trichloroethylene (3:5170), and tetrachloroethylene (3:5460) see (100).]

With $NH_4OH/CuCl$. Note that C̄ with $NH_4OH/CuCl$ does *not* give blue color within 5 min. (225) (dif. from pentachloroethane (3:5880) q.v.).

3:5750 (1) Paterno, Pisati, *Gazz chim. ital.* **1**, 463–464 (1871), *J. prakt. Chem.* (2) **4**, 175–178 (1871). (2) Mathews, *J. Am. Chem Soc.* **48**, 560 (1926). (3) Lecat, *Rec. trav. chim.* **45**, 624, ... *Belg.* **27**, 334–343 (1914); *Cent.* **1914**, I ... 774 (1926) (6) Timmermans, *Bull.* ... *physik. Chem.* **111**, 469 (1924). (8) ...) Breuer, *J. Am. Chem. Soc.* **58**, 1290 ... (12) Herz, Rathmann, *Chem. Ztg.* ... *hem.* **3**, 53 (1938). (14) Bell, *J. Chem.* ... *apan* **10**, 5–16 (1935). (16) Howell, ... *anorg. allgem. Chem.* **101**, 59 (1917). ... *soc. chim Belg.* **40**, 506–507 (1931). (19) Walden, Gloy, ... (20) Walden, Swinne, *Z. physik. Chem.* **82**, 281 (1913). ... 482–483 (1929). (22) Eckart, *Brennstoff-Chem.* **4**, 24–25 ... otton, Mouton, *Ann. chim.* (8) **28**, 236 (1913) (24) Veley, *Proc Roy. Soc. London*, B-**82**, 217–225 (1910). (25) Nelson, *Ind. Eng Chem.* **22**, 971 (1930). (26) Bates, Hazzard, Palmer, *Ind. Eng Chem.* **33**, 375–376 (1941). (27) van Arkel, Vles, *Rec. trav. chim.* **55**, 410 (1936). (28) Staverman, *Rec. trav. chim* **60**, 836–841 (1941); *Cent.* **1942**, ... Pfleiderer, *Z. anorg. allgem. Chem.* **124**, 68 (1922). ... *allgem. Chem* **137**, 87–90 (1924). ... **103**, 219 (1921/2). (32) Trividic, *Rev. gén. col-* ...) Jorissen, Meuwissen, *Rec trav. chim* **44**, 132–140 (1925) (34) Coward, Jones, *Ind. Eng Chem.* **18**, 970–974 (1926). (35) Jorissen, Velisek, *Rec trav. chim* **43**, 85–86 (1924). (36) Langen van der Valk, *Rec. trav chim.* **48**, 201–219 (1929). (37) Timmermans, *Bull soc chim. Belg* **36**, 187 (1927). (38) Timmermans, *Bull. soc. chim. Belg* **43**, 633 (1934). (39) Cohen, deMeester, Moesveld, *Z. physik. Chem.* **114**, 321–333 (1924); **108**, 104–107 (1924); *Rec. trav. chim.* **42**, 779–783 (1923). (40) Lecat, *Ann. soc. sci. Bruxelles* **48**, I, 119, 122 (1928).

(41) Lecat, "L'Azeotropism," 1918, p. 68 (42) Lecat, *Ann. soc. sci. Bruxelles* **49**, 21 (1929). (43) Othmer, White, Trueger, *Ind Eng Chem* **33**, 1242–1247 (1941). (44) Ralston, Ingle, McCorkle, *J. Org Chem.* **7**, 457–461 (1942). ... 9819, 9999–10003 (1919), *Cent.* **1919**, IV 413–4 ... (49) Stinchfield ... **17**, 341 (1923). ... ; *Cent.* **1926**, II 137; *C A.* **20**, 1522 (1926).

(51) Steindorff, Balle (to M.L B.), Ger. 365,286, Dec. 14, 1922; *Cent.* **1923**, II 922; not in *C.A.* (52) Bakelite Gesellschaft, Austrian 86,764, Dec. 27, 1921; *Cent.* **1922**, IV 714, not in *C.A.* (53) Youtz (to Standard Oil Co.), U.S. 2,031,145, Feb. 18, 1936, *Cent.* **1936**, II 898; *C.A.* **30**, 2408 (1936). (54) Boynton, U.S 1,715,589, June 4, 1929, *C A.* **23**, 3783 (1929): French ... *Chem Soc. Agron.* **33**, 759–761 (1941), *C.A.* **35**, 7637 (1941). (59) Elston (to du Pont Co.), U.S. 2,140,519, Dec. 20, 1938; *Cent.* **1939**, I 3247; *C A.* **33**, 2648 (1939). (60) Humphries, *Ann. Rept. Cacao Research* **8**, 38–39 (1938); *Cent.* **1939**, II 3355, *C A.* **34**, 588 (1940).

(61) McDonald, *6th Ann. Rept. Cacao Research* **1936**, 43–44; *Cent.* **1937**, II 3253; *C.A.* **32**, 969 (1938). (62) Wadsworth, *Analyst* **47**, 152–163 (1922), *Cent.* **1922**, IV 174; *C.A.* **16**, 1995 (1922). (63) Wadsworth, *Analyst* **46**, 32–37 (1921); *Cent.* **1921**, II 907; *C.A.* **15**, 1170 (1921).

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(71 ... Chem. Ztg. 53, 605 (1929). (73) van der Werth, *Chem. Ztg.* **52**, 23–24 (1928). (74) Lepper, *Z. Untersuch. Lebensm.* **59**, 79–81 (1930). (75) Lundin, *Chem. Ztg.* **55**, 762–763 (1931). (76) Metzger, *Landw. Jahrb. Schweiz* **45**, 625–632 (1931); *Cent.* **1932**, I 1287; *C.A.* **28**, 4006 (1934). (77) Tausz, Rumm, *Gas u. Wasserfach*, **71**, 417–420 (1928); *Cent.* **1928**, I 3019; *C.A.* **22**, 2651 (1928). (78) Friedrichs, *Chem. Ztg.* **53**, 287 (1929). (79) Berth, *Chem. Ztg.* **51**, 975–976 (1927). (80) Riesener, Kessen, *Chem. Ztg.* **52**, 243–244 (1928); *Cent.* **1928**, II 1052.

(81) Kingman, *Ind. Eng. Chem.* **18**, 93–94 (1926). (82) Tucker, Burke, *Analyst* **60**, 663–667 (1935). (83) Pritzker, Jungkunz, *Z. Untersuch. Lebensm.* **57**, 520–524 (1929). (84) Pritzker, Jungkunz, *Mitt. Lebensm. Hyg* **20**, 65–69 (1929); *Cent.* **1929**, II 609; *C.A.* **24**, 1315 (1930). (85) McConnell, *J. Am. Med. Assoc.* **109**, 762 (1937). (86) Forbes, *Brit. Med. J.* **1943**, I 348–350; *C.A.* **37**, 435 (1943). (87) Schwander, *Arch. Gewerbepath. Gewerbehyg.* **7**, 109–116 (1939); *Cent.* **1939**, II 1331; not in *C.A.* (88) Freitag, *Rayon Text. Monthly* **18**, 543–545 (1937); *Cent.* **1937**, II 3928; not in *C.A.* (89) Gasg, *Bull. trav. soc. pharm. Bordeaux* **75**, 87–101 (1937); *Cent.* **1937**, I 5006; *C.A.* **32**, 3047 (1938). (90) Bürgi, *Wien. klin. Wochschr.* **49**, 1545–1548 (1936); *Cent.* **1937**, I 3515; not in *C.A.*

(91) Barsoum, Saad, *Quart. J. Pharmacol.* **7**, 205–214 (1934); *Cent.* **1934**, II 2550; *C.A.* **28**, 6194 (1934). (92) Zangger, *Sammlung Vergiftungsfälle* ...
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II 279; not in *C.A.* (94) Müller, *Arch. Gewerbepath. G* ...
II 1449; not in *C.A.* (95) Zöllinger, *Arch. Gewerbepa* ...
1931, II 1450; not in *C.A.* (96) Lutz, *Arch. Gewerbep* ...
1931, I 2639; not in *C.A.* (97) Zangger, *Schweiz. med.* ...
(1931); not in *Cent.* (98) Zangger, *Schweiz. med. Wochschr.* **61**, 748–761 (1931); *C.A.* **26**, 3050 (1932); not in *Cent.* (99) Lutz, *Z. angew. Chem.* **43**, 807 (1930). (100) Barrett, Cunningham, Johnston, *J. Ind. Hyg. Toxicol.* **21**, 479–490 (1939).

(101) Wright, Schaffer, *Am. J. Hyg.* **16**, 374–380 (1932). (102) Mameli, Mossini, *Giorn. chim. ind. applicata* ...
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(111) Barrett, *J. Ind. Hyg. Toxicol.* **18**, 341 (1936). (112) Hanson, *Ind. Eng. Chem., Anal. Ed.* **13**, 119–123 (1941). (113) Thorpe, Whitely, "Dictionary of Applied Chemistry," 4th ed. (1937), **1**, 98–99. (114) Klebanskii, *Gosudarst. Inst. Prikladnoi Khim., Sbornik Statei* **1919–1939**, 359–383 (1939); *C.A.* **36**, 2521 (1942). (115) Favorskii, Margules, Davuidova, *Trans. State Inst. Applied Chem. (U.S.S.R.)* **24**, 47–54 (1935); *C.A.* **29**, 7271 (1935). (116) Suknevich, Khomutin, *Trans. State Inst. Applied Chem. (U.S.S.R.)* **24**, 54–66 (1935); *C.A.* **29**, 7271 (1935).
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(131) Chem. Fabrik Griesheim-Elektron, Ger. 204,883, Dec. 12, 1908; *Cent.* **1909**, I 325; *C.A.* **3**, 1457 (1909). (132) Ornstein, Ger 241,559, Dec. 5, 1911; *Cent.* **1912**, I 174; *C.A.* **6**, 2291 (1912). (133) Consortium für Elektrochem. Ind., Ger. 154,677, Oct 7, 1904; *Cent.* **1904**, II 1177; not in *C.A.* (134) Lidholm, Ger. 204,516, Nov. 25, 1908; *Cent.* **1909**, I 114; *C.A.* **3**,

(141) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 28, 1939; *Cent.* **1939**, II 1775; *C.A.* **33**, 5001 (1939). (142) Maze, U.S. 1,425,669, Aug. 15, 1922; *C.A.* **16**, 3314 (1923). (143) Michel, *Z. angew. Chem.* **19**, 1096 (1906). (144) Salzbergwerk Neu-Stassfurt, Ger. 174,068, Sept. 8, 1906, *Cent.* **1906**, II 1297; *C.A* **1**, 950 (1907). (145) Irvine, Haworth (to Carbide and Carbon Chem. Co), U.S. 1,496,675, June 3, 1924; *Cent.* **1924**, II 1511; [*C.A.* **18**, 2345 (1924)]. (146) Askenasy, Heller, Ger. 549,341, April 26, 1932; *Cent.* **1932**, II 287; *C.A.* **26**, 3807 (1932). (147) Maier, French 655,930, April 25, 1929; *Cent.* **1929**, II 1347, *C.A.* **23**, 3931 (1929). (148) Levine (to du Pont Co.), Can. 395,846, April 15, 1941; *C.A.* **35**, 4482 (1941); Brit. 505,196, Ju

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'68 (1938); *Cent.*

(161) Nicodemus, *J. prakt. Chem.* (2) **83**

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1909, II 2103, *C.A.* **4**, 812 (1910). (176) A. Wacker Soc. Elektrochem. Ind., Ger. 345,259, Dec. 8, 1921; [*Cent.* **1922**, II 413]; not in *C.A.*: Brit. 150,080, Jan. 27, 1921, *Cent* **1921**, II 1061; *C.A.* **15**, 1535 (1921). (077) Consortium für Elektrochem. Ind, Ger. 217,554, Jan. 17, 1910; *Cent.* **1910**, I 700, *C.A.* **4**, 1651 (1911). (178) Wiegand (to Chem. Fabrik von Heyden), Ger. 566,034, Dec. 14, 1932; *Cent* **1933**, I 1350; *C.A.* **27**, 1012 (1933). (179) Wiegand (to Chem. Fabrik von Heyden), Ger. 567,272, Dec. 31, 1932; *Cent.* **1933**, I 1842; *C.A.* **27**, 1365 (1933). (150) Schanejev, *Ann* **216**, 262 (1882).

(181) Müller, Lüber, *Ber.* **65**, 985–987 (1932). (182) Müller, Ehrmann, *Ber.* **69**, 2207–2210 (1936). (183) Guyot, Simon, *Compt. rend.* **170**, 736 (1920). (184) Biesalski, *Z. angew. Chem.* **37**, 307 (1924). (185) Miller, *J. Am. Chem Soc.* **62**, 341–342 (1940). (186) Swarts, *Cent.* **1903**, I 13. (187) Gruner (to Kali-Chemie, A.G.), Ger. 712,478, Oct. 21, 1941; *Cent.* **1942**, I 1053;

C.A. **37**, 4407 (1943). (188) Salzbergwerk Neu-Stassfurt, Ger. 248,982, July 6, 1912; *Cent.* **1912**, II 299; *C.A.* **6**, 2824 (1912). (189) Loiseau, French 565,356, Jan. 25, 1924; *Cent.* **1925**, II 1227; not in *C.A.* (190) Mkryan, Babayan, *Sbornik Trudov Armyanskogo Filiala Akad. Nauk* **1940**, No. 2, 51–58; *C.A.* **37**, 5694 (1943).

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Ward, *J. Chem. Soc.* **1934**, 2003. (206) Petrenko-Kritschenko, *Ber.* **61**, 853 (1928). (207) Huntress, Hershberg, unpublished results. (208) Consortium für Elektrochem. Ind. Ger. 257,878, March 22, 1913; *Cent.* **1913**, I 1373; *C.A.* **7**, 2836 (1913). (209) Metz, *J. prakt. Chem.* (2) **135**, 142–144 (1932). (210) Compagnie des Products Chimiques d'Alais et de la Camargue, Ger. 351,463, April 7, 1922; *Cent.* **1922**, IV 154; not in *C.A.*; Brit. 132,755, May 14, 1919; *C.A.* **14**, 285 (1920); Guyot, U.S. 1,313,716, June 15, 1920; *C.A.* **14**, 2344 (1920).

(211) Mkryan, *Sbornik Trudov Armyanskogo Filiala Akad. Nauk* **1940**, No. 2, 36–41; *C.A.* **37**, 5694 (1943). (212) Pogosyan, Mkryan, Russ. 50,533, Feb. 28, 1937; *Cent.* **1938**, II 412; *C.A.* **31**, 8549 (1937). (213) British Dyestuffs Corp., Levinstein, Imbert, Brit. 173,540, Feb. 2, 1922; French 527,554, Oct. 27, 1921; Swiss 93,576, March 16, 1922; *Cent.* **1922**, IV 761; *C.A.* **16**, 1435 (1922). (214) Gowing-Scopes, *Analyst* **39**, 7 (1914). (215) Formanek, *Chem. Obzor* **5**, 57–59 (1922); *Cent.* **1930**, II 976; *C.A.* **24**, 4492 (1930). (216) Staudinger, *Z. angew. Chem.* **35**, 658–659 (1922). (217) Lenze, Metz, *Z. ges. Schiess-u. Sprengstoff.* **27**, 255–258, 293–296, 337–340, 373–376 (1932). (218) Mouneyrat, *Bull. soc. chim.* (3) **19**, 499–500 (1898). (219) Harlow, Ross (to Dow Chem. Co.), U.S. 1,891,415, Dec. 20, 1932; *Cent.* **1933**, I 1682; *C.A.* **27**, 1890 (1933). (220) Whitmore, Thurman, *J. Am. Chem. Soc.* **51**, 1497 (1929).

(221) Binaghi, *Gazz. chim. ital.* **57**, 670, 675 (1927); *Cent.* **1928**, I 908–909; *C.A.* **22**, 573–574 (1928). (222) Swarts, *Bull. soc. chim.* (4) **25**, 146,168–170 (1919). (223) Sastry, *J. Soc. Chem. Ind.* **35**, 94–95 (1916). (224) Weber, *Chem. Ztg.* **57**, 836 (1933); *Cent.* **1933**, II 3889; *C.A.* **28**, 727 (1934). (225) Doughty, *J. Am. Chem. Soc.* **41**, 1129–1131 (1919). (226) Phillips, Enns, *J. Assoc. Official Agr. Chem.* **27**, 442–446 (1944). (227) Coyer, *Hahnemannian Monthly* **79**, 230–241 (1944); *C.A.* **38**, 3358 (1944). (228) Strosacker, Amstutz (to Dow Chem. Co.), U.S. 2,322,258, June 22, 1943; *C.A.* **38**, 114 [illegible] **7**, 399–403 (1937). (230) Rauscher, *Ind.* [illegible]

(231) Tzurikh, *Trans. State Inst. Ap* [illegible] 2 (1935); not in *Cent.* (232) Lehman, [illegible]); *C.A.* **31**, 477 (1937), not in *Cent.* (233 [illegible] 1235 (1934); *C.A.* **29**, 4326 (1935). (234) Igi, *J. Chem. Ind. Japan* **23**, 1217–1237 (1920); *C.A.* **15**, 2273 (1921). (235) Askenasy, Vogelsohn, *Z. Elektrochem.* **15**, 773 (1909). (236) Aten, *Chem. Weekblad* **19**, 352 (1922); *Cent.* **1922**, III 984; *C.A.* **16**, 3593 (1922).

3:5755 1,1-DICHLOROPROPANOL-2 $C_3H_6OCl_2$ **Beil. I - 363**

(β,β-Dichloroisopropyl alcohol; dichloromethyl methyl-carbinol) $CH_3—CH(OH)—CHCl_2$ I_1— I_2-(383)

B.P. 146–148° at 765 mm. (1) D_{22}^{22} **= 1.3334 (1)**

Moderately sol. aq., very sol. alc., ether.

[For prepn. of C̄ from dichloroacetaldehyde (3:5180) with MeMgBr in dry ether (57.4% yield) see (1); from 1,1-dichloropropanone-2 (*unsym.*-dichloroacetone) (3:5430) with anhydrous acetaldehyde + $Al(OEt)_3$ in dry ether (45% yield) see (2).] — [Note that the levorotatory stereoisomer of C̄, b.p. 146–148°, $[\alpha]_D = -9°$, has been obtd. (54% yield) from *unsym.*-dichloroacetone (3:5430) by reduction with yeast (3).]

[For behavior of C̄ with NaOEt in alc. or ether see (4).]

[C̄ with paraformaldehyde + $ZnCl_2$ gives (23.5% yield (5)) formaldehyde *bis*-(β,β-dichloroisopropyl)acetal [Beil. I-575], b.p. 81° at 0.2 mm. (4).]

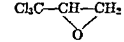
—— β,β-Dichloroisopropyl benzoate: oil, b.p. 92–94° at 0.15–0.17 mm. (4). [From C̄ with BzCl refluxed 4 hrs. at 150° (80% yield (4)).]

—— β,β-Dichloroisopropyl carbamate: unreported. [Note, however, that the corresp. deriv. of levorotatory C̄ (obtd. with carbamyl chloride in ether) has m.p. 61–63° (3).]

3:5755 (1) Wohl, Roth, *Ber.* **40**, 217–218 (1907). (2) Nord, Ger. 434,728, Oct. 5, 1926; *Cent.* **1926**, II 2845. (3) Sen, *J. Indian Chem. Soc.* **1**, 1–8 (1924/25); *Cent.* **1925**, I 537; *C.A.* **19**, 816 (1925); *Biochem. Z.* **151**, 51–53 (1924); *Cent.* **1924**, II 2272; *C.A.* **19**, 3277 (1925). (4) Wohl, *Ber.* **41**, 3606–3608 (1908).

3:5760 3,3,3-TRICHLORO-1,2-EPOXYPROPANE $C_3H_3OCl_3$ Beil. S.N. 2362

(ω,ω,ω-Trichloropropylene oxide)



B.P. 149° at 764 mm. (1)	$D_{25}^{25} = 1.4921$ (4)	$n_D^{25} = 1.4737$ (4)
149° at 750 mm. (2)		
49° at 11 mm. (1)	$D_4^{20} = 1.495$ (5)	$n_{He}^{20} = 1.4768$ (5)
44–45° at 13 mm. (2)		
41–42° at 10 mm. (3)	$D_4^{19} = 1.4962$ (5)	
39–40° at 11 mm. (4)		

Colorless mobile liq. with sweetish not unpleasant odor suggesting epichlorohydrin (3:5358). [Note that C̄ was at first (1) erroneously supposed to be 1,1,1-trichloroacetone (3:5620).]

[For prepn. of C̄ from chloral (3:5210) (1) (2) (4) or chloral hydrate (3:1270) (3) with diazomethane in ether (yields: 64% (2), 48% (4), 47.5% (3)) see indic. refs.]

C̄ does *not* (2) react with aq. *o*-nitrophenylhydrazine HCl or with aq. semicarbazide.

[C̄ with 5 pts. conc. aq. HCl evolves heat and by opening of epoxy ring yields (2) 1,1,1,3-tetrachloropropanol-2 (3:9036), b.p. 95–96° at 17 mm. (2). — C̄ with Ac_2O + trace sublimed $FeCl_3$ gives (2) in analogous fashion 3,3,3-trichloro-1,3-diacetoxypropane, b.p. 126–128° at 16 mm. (2).]

[C̄ with alcohols gives (3) corresp. alkoxymethyl-hemiacetals of chloral.]

[C̄ with MeMgI in dry ether at −15° gives (59% yield (4)) *1,1,1-trichloro-3-iodopropanol-2*, ndls. from pet. ether, m.p. 54–55° (4). — C̄ with MeLi in dry ether at −75° gives (85% yield (4)) 1,1,1-trichlorobutanol-2 (3:5955).]

3:5760 (1) Schlotterbeck, *Ber.* **42**, 2561 (1909). (2) Arndt, Amende, *Ber.* **61**, 1121–1122 (1928). (3) Meerwein, Bersin, Burneleit, *Ber.* **62**, 1002–1003, 1006–1009 (1929). (4) Gilman, Abbott, *J. Org. Chem.* **8**, 227–228 (1943). (5) von Auwers, *Ber.* **62**, 1319 (1929).

3:5765 METHYL β-CHLOROPROPIONATE $C_4H_7O_2Cl$ Beil. II - 250

$ClCH_2.CH_2.CO.O.CH_3$ II_1—

II_2-(227)

B.P. 148–150° at 760 mm. (1)	$D_4^{20} = 1.1634$ (7)	$n_D^{20} = 1.4265$ (7)
148° (2)		
40–42° at 10 mm. (3)	$D_4^{12} = 1.1874$ (1)	$n_D^{12} = 1.4319$ (1)

[For prepn. of C̄ from β-chloropropionic ac. (3:0460) by esterification with MeOH + HCl see (2) (3); from acrylic acid chloride (3:7153) + MeOH see (2) (4), from methyl

acrylate (1:3025) by addn. of HCl see (1), from acrylonitrile + HCl to β-chloropropionitrile followed by reactn. with MeOH (96% yield (5)) see (5).]

[Note that the b.p. of 155–157° reported by (4) has been characterized as erroneous (2) (1).]

C̄ on htg. with diethylaniline at abt. 200° gives (1) (78% yield (3)) methyl acrylate (1:3025), b.p. 80° (1).

[For study of acid hydrolysis of C̄ see (6).]

3:5765 (1) Moureu, Murat, Tampier, *Ann. chim.* (9) **15**, 214 (1921). (2) Moureu, *Ann. chim.* (7) **2**, 170–171 (1894). (3) Späth, Spitzy, *Ber.* **58**, 2276 (1925). (4) Henry, *Compt. rend.* **100**, 116 (1885); *J. prakt. Chem.* (2) **31**, 127 (1885). (5) British (to I.G.) 352,802, Aug. 6, 1931; *Cent.* **1931**, II 2658. (6) Palomaa, *Ber.* **74**, 1866–1870 (1941); *C.A.* **36**, 5413 (1942). (7) Schjanberg, *Z. physik. Chem.* **A-172**, 231 (1935).

3:5770 CYCLOHEXYL CHLOROFORMATE $C_7H_{11}O_2Cl$ Beil. S.N. 100
(Cyclohexyl chlorocarbonate) $C_6H_{11}.O.CO.Cl$

B.P. abt. 150° dec. (1)
87.5° at 27 mm. (1)
78–83° at 12 mm. (2)

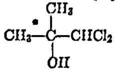
D_{20}^{20} = **1.1259** (1)

[For prepn. from cyclohexanol (1:6415) + phosgene (3:5000) see (1); for application in prepn. of textile auxiliaries see (3).]

Ⓓ Cyclohexyl carbamate: from C̄ + conc. aq. NH_4OH; m.p. 110° (2).

3:5770 (1) Kretov, Bakakina, *Zhur. Priklad. Khim.* **2**, 809–816 (1929); *C.A.* **24**, 1098 (1930); *Cent.* **1930**, I 2876. (2) Puyal, Montagne, *Bull. soc. chim.* (4) **27**, 862 (1920). (3) French 731,405, Sept. 2, 1932; *Cent.* **1933**, I 313.

3:5772 1,1-DICHLORO-2-METHYLPROPANOL-2 $C_4H_8OCl_2$ Beil. I - 382
(*unsym.*-Dichloro-*ter*-butyl alcohol, I₁—
dichloromethyl-dimethyl carbinol) I₂—



B.P.		M.P.		
151° (1)		+8° (4)	D_4^{19} = **1.2363** (4)	n_D^{19} = **1.4598** (4)
150.5° at 760 mm. (2)				
143.5° (3)			D_4^{0} = **1.2507** (4)	
52° at 10 mm. (4)				
38° at 5 mm. (4)				

[*See also the isomeric* 1,3-*dichloro-2-methylpropanol-2* (3:5977).]

PREPARATION OF C̄

[For prepn. of C̄ from 1-chloro-2-methylpropene-1 (β,β-dimethylvinyl chloride = "isocrotyl chloride") (3:7120) by addn. of HOCl with Cl_2 + aq., aq. HOCl, or even alkyl or alkaryl hypochlorites as directed see (2) cf. (5) (3).]

[For prepn. of C̄ from α,α-dichloroacetone (3:5430) with MeMgBr in ether see (1).]

[For prepn. of C̄ from ethyl dichloroacetate (3:5850) with MeMgBr (74% yield (4)) or MeMgI (63% yield (6)) cf. (4) or from methyl dichloroacetate (3:5655) with MeMgBr (7) see indic. refs.]

CHEMICAL BEHAVIOR OF $\bar{C}$

With inorganic reagents. $\bar{C}$ does *not* (1) react with aq. HCl. — $\bar{C}$ *cannot* (4) be hydrolyzed to the corresp aldehyde, viz., α-hydroxyisobutyraldehyde [Beil. I-829, I_2-(871)], either by aq., aq. Na_2CO_3, aq. $CaCO_3$, or aq. PbO.

[$\bar{C}$ with 5 *N* abs. alc. NH_3 in s.t. at 100° as directed gives (8) 2,2,5,5-tetramethyldihydropyrazine, m.p. 83–84° (8) (9).]

With organic reactants. [For behavior of $\bar{C}$ with $MeNH_2$ yielding a prod. of compn. $C_{16}H_{32}N_4$ see (8).]

[$\bar{C}$ with Me_2NH in C_6H_6 in s.t. at 130° not only introduces the dimethylamino group for one chlorine but also ring-closes with loss of HCl giving (52% yield (8)) 1-(dimethylamino)-2-methyl-1,2-epoxypropane (α,α-dimethyl-α'-(dimethylamino)ethylene oxide), b.p. 28–30° at 13 mm., $D_-^{22.5} = 0.8725$, $n_D^{22.5} = 1.4216$ (8).]

—— α-Hydroxyisobutyraldehyde di-β-naphthylacetal [$(CH_3)_2$-C(OH)CH$(O.C_{10}H_7)_2$]: [This cpd. which might be expected from $\bar{C}$ with sodium β-naphtholate is unreported; note that 1,3-dichloro-2-methylpropanol-2 (3·5977) with sodium β-naphtholate gives the corresp. di-β-naphthyl ether, m.p. 151–152°.]

—— *unsym.*-Dichloro-*ter*-butyl acetate: unreported.

—— *unsym.*-Dichloro-*ter*-butyl benzoate: unreported.

—— *unsym.*-Dichloro-*ter*-butyl *p*-nitrobenzoate: unreported.

—— *unsym.*-Dichloro-*ter*-butyl 3,5-dinitrobenzoate: unreported.

—— *unsym.*-Dichloro-*ter*-butyl carbamate: m.p. 122° (7). [Prepd. from *unsym.*-dichloro-*ter*-butoxy MgBr by treatment with phosgene (3:5000) followed by NH_4OH (7).]

(1881). (4) Avy, *Bull soc. chim.* (4) **49**, 12–18 (1931). (5) Burgin, Hearne, Rust, *Ind. Eng. Chem* **33**, 385–388 (1941). (6) Iositch, *J. Russ. Phys.-Chem. Soc.* **36**, 1551 (1906). (7) Yoder, *J. Am Chem Soc.* **45**, 478–479 (1923). (8) Avy, *Bull. soc. chim.* (4) **49**, 514–522 (1931). (9) Conant, Aston, *J. Am. Chem. Soc.* **50**, 2788 (1928).

3:5775 2,2,2-TRICHLOROETHANOL-1 $Cl_3C.CH_2OH$ $C_2H_3OCl_3$ Beil. I - 338, I_1-(170), I_2-(337)

(β,β,β-Trichloroethyl alcohol)

B.P.			M.P.	
151°	cor.	(1)	18° (5)	$D_{23.5}^{23.5} = 1.5500$ (2)
151°	at 737 mm.	(2)	17° (6)	
151°	sl. dec.	(3)		
149.5–150.5°	at 765 mm.	(4)		
149–150°	at 760 mm.	(4)		
148–150°	at 720 mm.	(5)		
111°	at 170 mm.	(6)		
94–97°	at 125 mm.	(3)		
67–68°	at 25 mm.	(7)		
58–60°	at 16 mm.	(8)		
55–56°	at 11 mm.	(9)		
52–51°	at 10 mm.	(10)		

Colorless when pure, but slightly brown if distilled at ord. press. — Sol. in 12 pts. aq., vol. with steam; miscible with alc. or ether. — Solid is very hygroscopic.

$\bar{C}$ is an important pharmaceutical. — [Although full consideration of its pharmacology is beyond the scope of this text, for studies and reviews of this aspect see (11) (12) (13) (14) (40).] — $\bar{C}$ in the organism is in part excreted (15) (16) as urochloralic acid [Beil. I-620].

PREPARATION OF $\bar{C}$

$\bar{C}$ is readily obtd. from trichloroacetaldehyde (chloral) (3:5210) by various types of reducing actions which are able to effect reduction of the aldehyde group without serious interference with the halogen atoms.

By use of various alcoholates. [For prepn. of $\bar{C}$ from chloral (3:5210) with $Al(OEt)_3$ in abs. EtOH (yields: 85% (17), 84% (3), 80% (18)) (6) (10) (19) cf. (23) see indic. refs.; with Al isopropylate in isopropyl alc. (20) in pres. of acetaldehyde (yield 72–87% (21)) see indic. refs.; with C_2H_5OMgBr (9), $(CH_3)_2CHOMgBr$ (9), or other metallic isopropylates (22) see indic. refs.]

By use of RMgX. [For formn. of $\bar{C}$ from chloral (3:5210) during reaction with MeMgBr (24), with EtMgBr (25) (4), with iso-AmMgBr (4), with cyclohexyl MgBr (26), and various other RMgBr cpds. (7) (25) (yields: 65% (25), 50–60% (4), 42–52% (26)) see indic. refs.]

By use of metal alkyls. [For formn. of $\bar{C}$ from chloral (3:5210) by use of $ZnEt_2$ (2) (27) or $AlEt_3$ cpd. with ether (88.5% yield (8)) see indic. refs.; note, however, that $SnEt_4$ is *not* (8) effective.]

By phytochemical agents. [For prepn. of $\bar{C}$ from chloral (3:5210) by reduction with fermenting yeast see (28) (5).]

By misc. methods. [For formn. of $\bar{C}$ from urochloralic acid [Beil. I-620] by hydrolysis with dil. mineral acid see (1); for formn. of $\bar{C}$ in small amts. from EtOH + Cl_2 see (29).]

CHEMICAL BEHAVIOR OF $\bar{C}$

WITH INORGANIC REACTANTS

Oxidation. $\bar{C}$ reduces Fehling's soln. on warming (2). — $\bar{C}$ with fumg. HNO_3 is oxidized to trichloroacetic acid (1) (2).

Behavior with alkalies. [$\bar{C}$ in conc. aq. NaOH first dissolves then gives a white ppt. of Na deriv. (33). — $\bar{C}$ with aq. KOH dissolves and soon afterward reacts vigorously yielding (2) various prods. including chloroacetic acid (3:1370), β,β,β-trichloroethoxyacetic acid [Beil. III-233], m.p. 69.5° (2), and formic acid (1:1005).]

Behavior with inorganic acid chlorides. [$\bar{C}$ with PCl_3 evolves HCl and yields (27) *tris*-(β,β,β-trichloroethyl) phosphite, b.p. 263°, no formation of 1,1,1,2-tetrachloroethane (3:5555) being evident. — $\bar{C}$ with PCl_5 at 140° evolves HCl yielding (27) *tris*-(β,β,β-trichloroethyl) phosphate, m.p. 73–74° (sublimes without decn.) accompanied by a trace of 1,1,1,2-tetrachloroethane (3:5555).]

[$\bar{C}$ with $SOCl_2$ gives (30) *bis*-(β,β,β-trichloroethyl) sulfite, b.p. 139.5–140° at 5 mm., m.p. 6–7°. — $\bar{C}$ with SO_2Cl_2 in pyridine at 100° gives (30) *bis*-(β,β,β-trichloroethyl) sulfate, m.p. 118.5–119.5° cor., also obtd. (30) by oxidn. of the preceding sulfite with acid $KMnO_4$ in acetone.]

Behavior with $AlBr_3$. [$\bar{C}$ with $AlBr_3$ in CS_2 (31) (32) undergoes replacement of chlorine by bromine yielding acc. to conditions β-bromo-β,β-dichloroethanol, m.p. 17.5 (32), m.p. 17.5° (32), or β,β-dibromo-β-chloroethanol, m.p. 50°, b.p. 80° at 8 mm. (32).]

With Organic Reactants

(See also below under derivatives.) — [C̄ with diazomethane in heptane (33), n-BuOH (34), or acetone (33) (but not in ether (33)), yields β,β,β-trichloroethyl methyl ether, b.p. 35–36° at 16 mm. (33).]

[C̄ with 2,3-dichlorodioxane-1,4 (3:9105) gives (50% yield (18)) 2-chloro-3-(β,β,β-trichloroethoxy)dioxane-1,4, m.p. 77–78°.]

[C̄ with BEt_3 at 150° evolves C_2H_6 and gives (44% yield (8)) β,β,β-trichloroethyl diethylborate, $CCl_3CH_2OB(C_2H_5)_2$, b.p. 78–79° at 12 mm. (8).]

—— β,β,β-**Trichloroethyl acetate**: oil, b.p. 167° sl. dec. at 736 mm. (2), 71° at 18.3 mm. (2), 88–91° (35), $D_{-}^{28} = 1.4239$ (35), $n_D^{28} = 1.4691$ (35). [From C̄ with AcCl in s.t. at 130° for several hrs. (2).]

—— β,β,β-**Trichloroethyl benzoate**: oil (29). [Note, however, that no constants are reported in the literature.]

Ⓓ β,β,β-**Trichloroethyl** m-**nitrobenzoate**: m.p. 75° (29) (26). [From C̄ + m-nitrobenzoyl chloride + aq. alk. (29).]

Ⓓ β,β,β-**Trichloroethyl** p-**nitrobenzoate**: m.p. 71° (28) (25). [From C̄ + p-nitrobenzoyl chloride + aq. alk. (28).]

Ⓓ β,β,β-**Trichloroethyl 3,5-dinitrobenzoate**: m.p. 142–143° (25).

Ⓓ β,β,β-**Trichloroethyl carbamate**: m.p. 64–65° (28) (36) (37) (38), 64° (39). [From C̄ (1 mole) with carbamyl chloride (1 mole) in dry ether (28) (note that C̄ with excess of carbamyl chloride gives (28) β,β,β-trichloroethyl allophanate, m.p. 182–183°), or from C̄ by treatment with phosgene (3:5000) followed by NH_3 (37). — Note that this prod. comprises the hypnotic pharmaceutical known as "Voluntal." It also forms molecular cpds. with various other pharmaceuticals; e.g., "Voluntal," m.p. 64–65° + pyramidone (2,3-dimethyl-4-dimethylamino-1-phenyl-pyrazolone-5) [Beil. XXV-452, XXV$_1$-(672)], m.p. 108°, give a 1:1 mol. cpd., m.p. 75–76°, known as "Compral"; for f.p./compn. data and diagrams on this (and similar systems) see (39).]

—— β,β,β-**Trichloroethyl** N-**phenylcarbamate**: m.p. 87° (39). [For f.p./compn. data and diagrams of this prod. (also known as N-phenylvoluntal) with antipyrine, etc., see (39).]

Ⓓ β,β,β-**Trichloroethyl** N-(α-**naphthyl**)**carbamate**: m.p. 120° (7), 119° (26). [From C̄ + α-naphthyl isocyanate at 120–135° for 2 hrs. (7).]

3:5775 (1) von Mering, *Z. physiol. Chem.* **6**, 487 (1882). (2) Garzarolli-Thurnlackh, *Ann.* **210**, 64–68 (1881). (3) Chalmers, *Org. Syntheses*, Coll. Vol. 2 (1st ed.), 598–601 (1943); **15**, 80–84 (1935). (4) Jotsitch, *J. Russ. Phys.-Chem. Soc.* **36**, 443–446 (1904), *Bull. soc. chim.* (3) **34**, 329–330 (1905). (5) Lintner, Lüers, *Z. physiol. Chem.* **88**, 122–123 (1913). (6) Callen (to Winthrop Chem. Co.), U.S. 1,725,054, Aug. 20, 1929; [*Cent.* **1930**, I 434], *C.A.* **23**, 4709 (1929): Ger. 437,160, Nov. 18, 1926; *Cent.* **1927**, I 802; not in *C.A.*: Brit. 286,797, April 5, 1928; *Cent.* **1928**, I 2750, *C.A.* **23**, 395 (1929). (7) Dean, Wolf, *J. Am. Chem. Soc.* **58**, 332–333 (1936). (8) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem.* (2) **147**, 236, 243 (1936). (9) Callsen (to I.G.), Ger. 565,157, Nov. 26, 1932; *Cent.* **1933**, I 1514; *C.A.* **27**, 992 (1933): Brit. 384,156, Dec. 22, 1932, *Cent.* **1933**, I 1351; [*C.A.* **27**, 4240 (1933)]. (10) Nakai, *Biochem. Z.* **152**, 272 (1924); *Cent.* **1925**, I 637, [*C.A.* **19**, 2807 (1925)].

[illegible]

[illegible]), U.S. 1,572,742, Feb. 9, 1926, [illegible] 27, 1926; [*Cent.* **1926**, II

1097]; *C.A.* **20**, 917 (1926). (20) Callsen (to I.G.), Ger. 489,281, Jan. 15, 1930; *Cent.* **1930**, I
1929, I 1741; *C.A.* **23**, 852 (1929).
in *C.A.* (22) I.G., Brit. 370,490,
(23) Dworzak, *Monatsh.* **47**, 12-
hem. *Soc.* **63**, 2306–2307 (1941).
Floutz, *J. Am. Chem. Soc.* **65**,
2255 (1943). (27) Delacre, *Bull. soc. chim* (2) **48**, 784–788 (1887). (28) Willstätter, Duisberg, *Ber.* **56**, 2284–2285 (1923). (29) Altschul, Meyer, *Ber.* **26**, 2758 (1893). (30) Sporzynski, *Arch. Chem. Farm.* **2**, 243–247 (1935); *Cent.* **1935**, II 2941; *C.A.* **30**, 5938 (1936).

(31) Muller (to Winthrop Chem. Co.), U.S. 2,057,964, Oct. 20, 1936; *C.A.* **31**, 112 (1937); not in *Cent.*: Brit. 366,581, March 3, 1932; *Cent.* **1932**, II 770; [*C.A.* **27**, 1893 (1933)]. (32) Schranz, Göth, Kühn, Kayser, Ger. 600,769, July 31, 1934; *Cent.* **1934**, II 2285; [*C.A.* **28**, 7429 (1934)]. (33) Meerwein, Bersin, Burneleit, *Ber.* **62**, 1006–1007 (1929). (34) Meerwein, Hinz, *Ann.* **484**, 23 (1930). (35) Baum, Vogt, Hennion, *J. Am. Chem. Soc.* **61**, 1458 (1939). (36) Willstätter, Straub, Hauptmann, *Münch. med. Wochschr.* **69**, 1651–1654 (1922); *Cent.* **1923**, I 1196; not in *C.A.* (37) F. Bayer & Co., Ger. 358,125, Sept. 4, 1922; *Cent.* **1922**, IV 888; *C.A.* **17**, 2172 (1923). (38) Mentzel, *Pharm. Zentralhalle* **63**, 579–580 (1922); **64**, 10–11 (1923); *Cent.* **1923**, II 549. (39) Pfeiffer, Seydel, *Z. physiol. Chem.* **178**, 81–96 (1928). (40) Burtner, Lehmann, *J. Pharmacol.* **63**, 183–192 (1938); *C.A.* **32**, 6741 (1938).

3:5780 β-CHLOROETHYL CHLOROFORMATE $C_3H_4O_2Cl_2$ Beil. III - 11

(β-Chloroethyl chlorocarbonate) $ClCH_2CH_2.O.CO.Cl$ III_1—

III_2-(10)

B.P. 152.5° at 752 mm. (1) D_4^{20} **= 1.3825 (1)** n_D^{20} **= 1.4465 (1)**

Colorless lachrymatory liq. which fumes in air. — Insol. aq., eas. sol. alc., ether.

[For prepn. from β-chloroethanol (ethylene chlorohydrin) (3:5552) + phosgene (3:5000) see (1).]

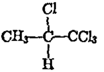
$\bar{C}$ on slight warming with quinoline dec. at 41–42° into ethylene dichloride (3:5130) + CO_2 (2).

$\bar{C}$ is readily hydrolyzed by warm aq. or dil. alk. to β-chloroethanol (3:5552) + CO_2 + HCl (1).

- Ⓓ β-Chloroethyl carbamate: from $\bar{C}$ + 2 moles conc. aq. NH_4OH; m.p. 76° (3) (4) (5). [The value of 115° given in Beil. III-11 is wrong (5).]
- Ⓓ β-Chloroethyl *N*-phenylcarbamate: from $\bar{C}$ in C_6H_6 added to C_6H_6 soln. of aniline (2 moles); after filtering off the pptd. aniline hydrochloride, the C_6H_6 is evapd. (6); white ndls., m.p. 51° (3). [This deriv. on short boilg. with dil. aq. or alc. alk. loses HCl and by ring closure yields 3-phenyloxazolidone-2 [Beil. XXVII-136], lfts. from alc., m.p. 124° (3), 122° (7).]
- Ⓓ β-Chloroethyl *N*-*p*-tolycarbamate: white ndls. from C_6H_6, m.p. 45° (6). [On treatment with alk. this gives 3-(*p*-tolyl)oxazolidone-2, white ndls. from alc., m.p. 91° (6).]
- Ⓓ β-Chloroethyl phenylcarbazate: from $\bar{C}$ on treatment with 1 mole phenylhydrazine in aq. pyridine; the red oil initially formed soon solidifies and is recrystd. from C_6H_6; white ndls., m p. 89° (8).

3:5780 (1) Nekrassow, Komissarow, *J. prakt. Chem.* (2) **123**, 163 (1929). (2) Carré, *Bull. soc. chim.* (5) **3**, 1069 (1936). (3) Nemirowsky, *J. prakt Chem.* (2) **31**, 174–175 (1885). (4) Ger. 387,963, Jan. 1, 1924; *Cent.* **1924**, II 403. (5) Kuroda, *Cent.* **1927**, II 243. (6) Adams, Segur, *J. Am. Chem. Soc.* **45**, 787–789 (1923). (7) Otto, *J. prakt. Chem.* (2) **44**, 17 (1891). (8) Dox, *J. Am. Chem. Soc.* **48**, 1952 (1926).

3:5785 1,1,1,2-TETRACHLOROPROPANE (β,β,β-Trichloroisopropyl chloride) $C_3H_4Cl_4$ Beil. I - 107, I_1—, I_2—



B.P.		F.P.		
152–153° cor.	at 760 mm. (1)	−65° (1)	D_{22}^{22} = 1.4695 (6)	n_D^{20} = 1.4855 (6)
150–151°	at 751 mm. (6)	−64° (6)	D_{20}^{20} = 1.473 (1)	n^{-} = 1.4867 (1)
87–88°	at 104 mm. (6)			

Colorless liq. insol. aq. [For use as dry-cleaning solvent see (2).]

[For prepn. of $\bar{C}$ from 1,1,1-trichloropropanol-2 (3:0846) via reactn. with PCl_3 and action of Cl_2 on this product see (1), for prepn. of $\bar{C}$ with 1,1-dichloropropene-1 (3:5120) + Cl_2 + cat at 0–30° in absence of light see (3) (4); from 3,3,3-trichloropropene-1 (3:5345) by addn. of HCl in pres. of 3% $FeCl_3$ in s.t. at 50° for 50–100 hrs. see (6).]

$\bar{C}$ with aq. or alc. NaOH or KOH for 3 hrs. at 95° gives (93% yield (5)) 1,1,2-trichloropropene-1 (3:5395), b p. 118° (5).

3:5785 (1) Henry, *Rec. trav. chim* 24, 333–334 (1905). (2) Sh[illegible]
Cent. 1935, II 3859, *C.A* 29, 6440 (1935). (3) Cass (to du P[illegible]
Cent. 1938, I 1218, *C.A.* 32, 194 (1938). (4) du Pont Co. & [illegible]
Cent. 1938, I 1218; *C.A.* 32, 958 (1938). (5) du Pont Co. & [illegible]
Cent. 1938, I 1218, *C.A.* 32, 596 (1938). (6) Kharasch, Ros[illegible]
2558–2560 (1941).

3:5800 METHYL TRICHLOROACETATE $C_3H_3O_2Cl_3$ Beil. II - 208, II_1—, II_2-(190)

$Cl_3C.COOCH_3$

B.P.		F.P.		
153.8°	at 760 mm. (1)	−17.5° (1)	D_4^{20} = 1.4874 (8)	n_D^{20} = 1.4572 (8)
153°	(2)		1.4864 (7)	1.45717 (7)
152.3–152.5°	at 765.3 mm. (3)			
150.0–150.5°	at 679 mm. (4)			
52–54°	at 12 mm. (5)			
41.5–41.6°	at 12 mm. (6)			
46.5–47.0°	at 11 mm. (7)			

[For prepn. of $\bar{C}$ from trichloroacetic acid (3:1150) with MeOH at 60° (50–66% yield (2)), with MeOH + HCl at 50° (74.6% yield (2)), with MeOH + H_2SO_4 (9), with MeOH + $BF_3.Et_2O$ at 64° (73% yield (2)), or with Me_2SO_4 in s.t. at 200° (10) see indic. refs.; from trichloroacetamide + MeOH + BF_3 (53% yield) see (2); from "tetrachloroethylidene trichlorolactate" [Beil. XIX-105] with MeOH see (5).]

[For studies on hydrolysis of $\bar{C}$ under various circumstances see (11) (6) (7) (12).]

[For speed of reactn. with pyridine at 18–20° see (13).]

3:5800 [illegible] (3) Toole, Sowa, *J. Am. Chem.*
[illegible] (4) Sudborough, Karve,
[illegible] (5) Anschütz, Haslam,
[illegible] Palomaa, Salmi, Korte,
Ber. 72, 790–797 (1939). (8) Schjanberg, *Z. physik. Chem.* A-172, 229 (1935). (9) Dumas, *Ann.* 32, 111 (1839). (10) Simon, *Compt. rend.* 176, 585 (1923).
(11) Olivier, Berger, *Rec. trav. chim* 41, 642 (1921); 44, 643, 647–648 (1925). (12) Salmi, Suonpää, *Ber.* 73, 1126–1131 (1940). (13) Tronov, Akivis, Orlova, *J. Russ. Phys.-Chem. Soc.* 61, 345–353 (1929); *Cent.* 1929, II 2550; *C.A.* 24, 590 (1930).

3:5820 3-CHLOROPROPEN-2-OL-1 (γ-Chloroallyl alcohol) $CH=CH-CH_2$ (Cl on C-1, OH on C-3) C_3H_5OCl Beil. I-439, I_1—, I_2—

High-boiling stereoisomer	B.P. 153.0° at 756 mm. (1)	$D_4^{15} = 1.1582$ (1)	$n_D^{15} = 1.4600$ (1)
		$D_4^{25} = 1.1681$ (1)	$n_D^{25} = 1.4611$ (1)
		$D_4^{20} = 1.1720$ (1)	$n_D^{20} = 1.4661$ (1)
Low-boiling stereoisomer	B.P. 140.3° at 746 mm. (1)	$D_4^{35} = 1.1623$ (1)	$n_D^{35} = 1.4573$ (1)
		$D_4^{25} = 1.1720$ (1)	$n_D^{25} = 1.4617$ (1)
		$D_4^{20} = 1.1760$ (1)	$n_D^{20} = 1.4638$ (1)

Colorless liquids; both stereoisomers possess a delayed vesicant actn., and care should be taken in handling them.

[For prepn. of Č from 1,3-dichloropropene-1 (γ-chloroallyl chloride) (3:5280) by hydrolysis for 2 hrs. under reflux with aq. 10% Na_2CO_3 (10% excess over 1 equiv.) see (1); note that the high-boiling stereoisomer of γ-chloroallyl chloride gives (76% yield) of the high-*boiling Č, and that the lower-boilg. stereoisomer of γ-chloroallyl chloride gives (81% yield)* the lower-boiling stereoisomer of Č (1).—Note that from γ-chloroallyl acetate (which was presumably a mixture of the acetates of both stereoisomers of Č) by hydrolysis with cold aq. NaOH Č (presumably a mixt. of stereoisomers) has been reported (2).]

The two stereoisomers of Č behave differently with hot aq. NaOH (1): the higher-boilg. stereoisomer fails to give any propargyl alcohol but some acetylene and sodium formate are formed; the lower-boiling stereomer on refluxing with aq. 12.5% NaOH (10% excess) for 3 hrs. gives (by dehydrochlorination) 69% yield of propargyl alcohol (propyne-1-ol-3) [Beil. I-451], b.p. 114-115° (for study of influence of NaOH concn. and time see (1)).

① **γ-Chloroallyl *N*-phenylcarbamate:** ndls. from pet. ether, m.p. 75° (2). [From Č + phenyl isocyanate (note, however, that the Č employed very probably was a mixt. of the two stereoisomers (2)).]

3:5820 (1) Hatch, Moore, *J. Am. Chem. Soc.* **66**, 285-287 (1944). (2) Kirrmann, Pacaud, Dosque, *Bull. soc. chim.* (5) **1**, 868 (1934).

3:5825 1,1,2,2-TETRACHLOROPROPANE $CH_3-CCl_2-CHCl_2$ $C_3H_4Cl_4$ Beil. I-107, I_1—, I_2—

B.P. 153-154° (1)
153° (3)

$D_{13}^{13} = 1.47$ (1)

Liquid; misc. with alc. or ether; insol. aq.

[For prepn. of Č from α,α-dichloroacetone (3:5430) + PCl_5 see (3); from 1,2-dichloropropene-1 (3:5150) by addn. of Cl_2 see (1); for formn. of Č in small amt. as by-product of actn. of Cl_2 on propylene see (2).]

Č with warm alc. KOH, or with alc. NH_3 at 140° splits off HCl yielding (3) (1) 1,1,2(?)-trichloropropene-1, (3:5305), b.p. 115° (3), 116-117° (1).

3:5825 (1) Szenic, Taggesell, *Ber.* **28**, 2667-2668 (1895). (2) Goudet, Schenker, *Helv. Chim. Acta* **10**, 136 (1927). (3) Borsche, Fittig, *Ann.* **133**, 114-117 (1865).

3:5835 **1,4-DICHLOROBUTANE** $CH_2CH_2.CH_2.CH_2$ (Cl on first and last C) $C_4H_8Cl_2$ Beil. I - 119
(Tetramethylene I₁-(38)
(di)chloride) I₂-(81)

B.P.		M.P.		
155°	at 760 mm. (1) (6)	−38.7° (4)	D_4^{20} = 1.1598 (2)	n_D^{20} = 1.4566 (2)
74.7°	at 50 mm. (2)			
53–58°	at 12 mm. (3)			

The b p. of 163° (3) is erroneous (1).

[For prepn. from *N*-benzoylpyrrolidine [Beil. XX-5] + PCl_5 see (3); from *N,N'*-dibenzoyltetramethylenediamine + PCl_5 see (5); from butanediol-1,4 (tetramethylene glycol) (1:6516) + $SOCl_2$ see (10); from 1-chlorobutane by chlorination in light (together with other products) see (2) (7) (8) (9); from tetrahydrofuran [Beil. XVII-10, $XVII_1$-(5)] with HCl gas in pres. of 50% $ZnCl_2$ (59% yield) see (15) [note that in absence of $ZnCl_2$ only 4-chlorobutanol-1 (3:9170) is formed (15) (16).]]

[C̄ on passing over alkali (NaOH, K_2CO_3, soda-lime, etc.) at elevated temperatures (e.g., 700–750°) yields butadiene-1,3.] [For studies of this reaction see (7) (8) (9).]

C̄ can be hydrolyzed to tetramethylene glycol (1:6516) only very slowly (6).

C̄ htd. with p-toluidine (3 moles) at 100° for 10 hrs. gives (70% yield (11)) *N-p*-tolylpyrrolidine, b.p. 120° at 8 mm., cryst. from dil. alc., m.p. 42° (11). [For corresp. behavior with aniline yielding *N*-phenylpyrrolidine see (12).]

—— **1,4-Diphthalimidobutane:** obtd. indirectly (13) and as by-product (14) of prepn. of *N*-(δ-chloro-*n*-butyl)phthalimide; pr. from AcOH, m.p. 219° (13).

3:5835 (1) Hass, *J. Chem. Education* **13**, 493 (1936). (2) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 893–896 (1937); *C.A.* **31**, 5755 (1937); *Cent.* **1938**, II 2575. (3) von Braun, Beschke, *Ber.* **39**, 4361 (1906). (4) Timmermans, *Bull. soc. chim. Belg* **31**, 390 (1922). (5) von Braun, Lemke, *Ber.* **55**, 3530 (1922). (6) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1380–1388 (1939), *C A* **34**, 1611 (1940). (7) Muskat, Northrup, *J. Am. Chem. Soc* **52**, 4050–4052 (1930). [illegible]
3912 (19[illegible]
C.A. **31**, [illegible]
[illegible] *m Chem. Soc.*
(1939). (14)
(1941). (16)

3:5840 **1,2,3-TRICHLOROPROPANE** $CH_2—CH—CH_2$ (Cl on each C) $C_3H_5Cl_3$ Beil. I - 106
(Glycerol trichlorohydrin; I₁-(31)
" trichlorohydrin ") I₂-(73)

B.P.		F.P.		
[158°	(1)]	−14.7° (2)	D_4^{20} = 1.394 (7)	n_D^{20} = 1.4858 (5)
157°	(6)			
156.85°	(2)		D_4^{15} = 1.417 (8)	
156.0° at 760 mm.	(3)			
151–156°	(4)			
151.6–155.6° at 738 mm.	(5)			

[For prepn. of C̄ from glycerol (1:6540) with 3 moles $SOCl_2$ + 3 moles pyridine at 110–120° (78% yield) see (9); from either 1,3-dichloropropanol-2 (glycerol α-dichlorohydrin) (3:5985) or 2,3-dichloropropanol-1 (glycerol β-dichlorohydrin) (3:6060) with PCl_5 see

(10) (11); from 1,3-dichloropropanol-2 (see above) with $POCl_3$ at 180° (but only as by-prod.) see (12), or with $SOCl_2$ + diethylaniline see (13); from allyl chloride (3:7035) with Cl_2 (6) or with SO_2Cl_2 (80–90% yield (14)) see indic. refs.; from allyl iodide (15) or isopropyl iodide (8) (16) with Cl_2 see indic. refs.; from propane + Cl_2 see (17) (16); from 1,2-dichloropropane (propylene dichloride) (3:5200) with Cl_2 + Fe in ultra-violet light at −18° (18) (19) or with SO_2Cl_2 in pres. of org. peroxides (26) cf. (27) see indic refs.; from propylene with Cl_2 in gas phase in dark in absence of Fe see (20).

$\bar{C}$ on htg. with 20 pts. aq. in s.t. at 160° (11) or with aq. $NaHCO_3$ + Cu under press. at 130° for 5–6 hrs. (21) or with steam over cat. at 550–850° (25) yields glycerol (1:6540).

$\bar{C}$ on warming with solid KOH loses HCl yielding (22) mainly 2,3-dichloropropene-1 (3:5190) together with some 1,3-dichloropropene-1 (3:5280).

[$\bar{C}$ with alc. KSH yields (23) trithioglycerol [Beil. I-519] cf. (24).]

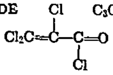
[$\bar{C}$ with $SbCl_5$ at 190° yields (6) 1,1,2,3-tetrachloropropane (3:6035).]

3:5840 (1) Carius, *Ann.* **124**, 223 (1862). (2) Timmermans, *Bull. soc. chim. Belg.* **30**, 67 (1921). (3) Gibson, *J. Soc. Chem. Ind.* **50**, 950 (1931). (4) Herzfelder, *Ber.* **26**, 1259 (1893). (5) Kohlrausch, Ypsilanti, *Z. physik. Chem.* **B-32**, 416 (1936). (6) Herzfelder, *Ber.* **26**, 2435 (1893). (7) Blanchard, *Bull. soc. chim.* (4) **43**, 1198 (1928). (8) Linneman, *Ann.* **136**, 48 (1865). (9) Carré, Mauclere, *Bull. soc. chim.* (4) **49**, 1152 (1931). (10) Fittig, Pfeffer, *Ann.* **135**, 359 (1865).

(11) Berthelot, Luca, *Jahresber.* **1857**, 477. (12) Hill, Fischer, *J. Am. Chem. Soc.* **44**, 2588 (1922). (13) Darzens, *Compt. rend.* **152**, 1314 (1911). (14) Kharasch, Brown, *J. Am. Chem. Soc.* **61**, 3432–3434 (1939). (15) Oppenheim, *Ann.* **133**, 383–384 (1865). (16) Berthelot, *Ann.* **155**, 108 (1870). (17) Schorlemmer, *Ann.* **152**, 159–163 (1869). (18) Cass, Levine (to du Pont Co.) Brit. 471,188, Sept. 30, 1937; *Cent.* **1938**, I 1218; *C.A.* **32**, 957 (1938). (19) Friedel, Silva, *Zeit. für. Chemie* **1871**, 683. (20) Laughlin, Brown (to Standard Oil Development Co.), U.S. 2,300,159, Oct. 27, 1942; *C.A.* **37**, 1725 (1943).

(21) Matter, Ger. 369,502, Feb. 20, 1923; *Cent.* **1923**, II 742. (22) Reboul, *Ann. chim.* (3) **60**, 38–40 (1860). (23) Ref. 1, pp. 236–240. (25) Lillienfeld, Brit. 385,980, *Feb. 2, 1933; Cent.* **1933**, 1928. (25) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932; *Cent.* **1932**, I 2994. (26) Kharasch, Brown, *J. Am. Chem. Soc.* **61**, 2145 (1939). (27) Zellner (to Tide Water Associated Oil Co.) U.S. 2,370,342, Feb. 27, 1945; *C.A.* **39**, 3535 (1945).

3:5845 TRICHLOROACRYLOYL CHLORIDE



C_3OCl_4

Beil. II —
II_1-(187)
II_2—

B.P. 158° at 760 mm. (1) (2) $n_D^{18.5}$ = 1.52709 (2)

[For prepn. of $\bar{C}$ from trichloroacrylic acid (3:1840) with $SOCl_2$ (2½ moles) refluxed for 12 hrs. (80–90% yield) see (2) cf. (6).]

$\bar{C}$ with $AlCl_3$ in CS_2 gives (1) a very stable 1:1 addn. prod.; on htg. it does *not* lose CO but ultimately decomposes giving (1) trichloroacetic acid (3:1150).

$\bar{C}$ with C_6H_6 + $AlCl_3$ gives (100% yield (1)) (3) phenyl α,β,β-trichlorovinyl ketone [Beil. VII_1-(190)], oil, b.p. 138° at 2 mm. (2), D_4^{25} = 1.3902 (2); n_D^{25} = 1.5798 (2); for analogous behavior of $\bar{C}$ with toluene + many other arom. hydrocarbons + $AlCl_3$ see (2).

[$\bar{C}$ with 3% H_2O_2 + 25% aq. NaOH at −3° to 0° gives (69% yield (3)) *cis*-(trichloroacryloyl) peroxide, cryst. from alc., m.p. 49°.]

Ⓓ Trichloroacrylic acid amide: m.p. 97° (4), 96–97° (5 ... [From $\bar{C}$ with aq. NH_4OH (5) or from ethyl trichloroacrylate ... — [For ... graphic study see (4).]

—— Trichloroacrylic anilide: ndls. from pet ... from $\bar{C}$ (1 ... with aniline (2 moles) in $CHCl_3$ at 0° (7 ...

—— Trichloroacrylic *p*-toluidide: ...

3:5845 (1) Böeseken, Hasselbach, *Rec. trav. chim.* **32**, 10–11 (1913). (2) Böeseken, Dujardin, *Rec. trav. chim.* **32**, 101–111 (1913). (3) Böeseken, Gelissen, *Rec. trav. chim.* **43**, 266–268 (1924). (4) Gilta, *Bull. soc. chim. Belg.* **39**, 587–588 (1930). (5) Fritsch, *Ann.* **297**, 317–318 (1897). (6) Bergmann, Haskelberg, *J. Am. Chem. Soc.* **63**, 1438 (1941).

3:5850 ETHYL DICHLOROACETATE $C_4H_6O_2Cl_2$ Beil. II - 203

$Cl_2CH.COOC_2H_5$ II_1-(91) II_2-(196)

B.P.	158.3–158.7°		(1)
	158–158.2°	cor.	(2)
	157.7°	at 754.6 mm.	(3)
	157°		(4)
	156°	at 738.2 mm.	(5)
	154–155°	at 749.5 mm.	(6)

[For prepn. of C̄ from dichloroacetic acid (3:6208) with EtOH + HCl see (7) (8); from chloral (3:5210) or chloral hydrate diacetate with EtOH/KCN (88% and 80% yield, respectively) see (4); from chloral cyanohydrin with abs. EtOH + conc. KOH (8) or abs. EtOH + anhyd. NaOAc (9) see indic. refs.; from tetrachloroethylene (3:5460) with NaOEt in s.t. at 100–120° see (10); from α,β-dichlorovinyl ethyl ether (3:5540) with Cl_2 followed by aq. see (11); from β,β-dichloro-α-acetoxyacrylonitrile with EtOH in s.t. at 150° see (12); for formn. of C̄ in reactn. of EtOH with Cl_2 see (13).]

C̄ on boilg. with alc. KOH yields (14) glycolic acid (1:0430) and oxalic acid (1:0445); C̄ on htg. with NaOEt in abs. alc. yields (15) a small amt. ethyl diethoxyacetate together with larger amts. of diethyl oxalo-chloroacetate diethylacetal on its decn. products.

[C̄ on boilg. with EtOH + KCN yields (16) K dichloroacetate, AcOH, and oxalic acid; C̄ on boilg. with EtOH + KF yields (17) KCl, SiF_4 + ethyl glyoxylate.]

[C̄ in ether treated with Na or htd. with Ag yields (18) diethyl maleate (1:3791).]

C̄ on shaking with aq. + benzylamine yields (19) N-benzyl-dichloroacetamide, m.p. 94.8–95.6° cor. (19), 95–96° (20).

C̄ on hydrolysis with acid yields EtOH (1:6130) + dichloroacetic acid (3:6208). [For study of kinetics of this hydrolysis see (21) (22) (23).]

(10) Fischer, Geuther, *Jahresber.* **1864**, 316.

(11) Crompton, Triffitt, *J. Chem Soc.* **119**, 1874–1875 (1921). (12) Kotz, *J prakt. Chem.* (2) **103**, 232 (1921/22). (13) Altschul, Meyer, *Ber.* **26**, 2757 (1893). (14) Claus, *Ber.* **14**, 1066 (1881) (15) Cope, *J Am. Chem. Soc.* **58**, 570–572 (1936). (16) Claus, *Ber.* **11**, 496–498; 1043–1044 (1878). (17) Swarts, *Cent* **1903**, I 14. (18) Tanatar, *Ber.* **12**, 1564 (1879). (19) Buehler, Mackenzie, *J. Am. Chem. Soc.* **59**, 421–422 (1937). (20) Mannich, Kuphal, *Arch. Pharm.* **250**, 544 (1912).

(21) Newling, Hinshelwood, *J. Chem. Soc.* **1936**, 1357–1361. (22) Timm, Hinshelwood, *J. Chem. Soc.* **1938**, 862–869. (23) Salmi, Suonpaä, *Ber.* **73**, 1126–1131 (1940).

3:5860 *d,l*-α-CHLORO-*n*-VALERYL CHLORIDE $C_5H_8OCl_2$ Beil. II - 302

$CH_3\,CH_2\,CH_2.\underset{Cl}{CH}-\underset{Cl}{C}{=}O$ II_1— II_2—

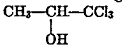
B.P. 155–157° at 763 mm. (1) $D_-^- = 1.246$ (1)

[For prepn. of C̄ from α-chloro-*n*-valeric acid (3:8783) with PCl_3 at 70–80° see (1).]

$\bar{C}$ on hydrolysis with aq. yields (1) α-chloro-*n*-valeric acid (3:8783), b.p. 222°.

3:5860 (1) Servais, *Rec. trav. chim.* **20**, 46–47 (1901).

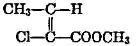
—— **1,1,1-TRICHLOROPROPANOL-2** $C_3H_5OCl_3$ Beil. I -(365)
I_1-(185)
I_2-(385)



B.P. 161.8° at 774 mm. **M.P. 50°**

See 3:0846. *Division A: Solids.*

3:5870 METHYL α-CHLOROCROTONATE $C_5H_7O_2Cl$ Beil. II - 414
II_1-(189)
II_2-(395)



B.P. 161–162° (1)	$D_4^{23.7} = 1.1570$ (1)		
161.5–161.7° at 762 mm. (2)	$D_4^{23.1} = 1.1575$ (1)	$n_D^{23.1} = 1.45689$ (1)
161° (3)		
160.8° (4)	$D_4^{22.6} = 1.1587$ (2)	$n_D^{22.6} = 1.45634$ (2)
158–159° (5)	$D_4^{20} = 1.160$ (1)	
59.0–59.5° at 16 mm. (5)	$D_-^{19} = 1.166$ (5)	$n_-^{19} = 1.455$ (5)

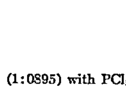
Note that the stereoisomeric methyl α-chloroisocrotonate is unreported.

[For prepn. of $\bar{C}$ from α-chlorocrotonic acid (3:2760) in MeOH with HCl gas (65% yield (5)) (1) (4); from α,α,β-trichloro-*n*-butyraldehyde (butylchloral) (3:1905) (as hydrate) in MeOH below 15° with KCN (2 moles) (85% yield (3)); or from methyl α-chloro-α-vinylacetate (5) by isomerization with NaOAc/AcOH on refluxing 30–40 hrs. (5) see indic. refs.]

$\bar{C}$ is unaffected by AgOH (dif. from methyl α-chloro-α-vinylacetate (5)).

3:5870 (1) von Auwers, *Ber.* **45**, 2806 (1912). (2) Eisenlohr, *Ber.* **42**, 3208 (1911). (3) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1045. (4) Kahlbaum, *Ber.* **12**, 343–344 (1879). (5) Rambaud, *Bull. soc. chim.* (5) **1**, 1353–1354 (1934).

3:5875 FUMARYL (DI)CHLORIDE $C_4H_2O_2Cl_2$ Beil. II - 743
II_1-(302)
II_2-(639)



B.P. 161–164°	(1)	$D_4^{20} = 1.408$ (3)	$n_D^{18.1} = 1.50038$ (3)
160°	(2)		
158–160°	(3)	$D_4^{16.8} = 1.4117$ (3)	
76° at 33 mm.	(4)		
59° at 16 mm.	(5)		
60° at 14 mm.	(6)		
62–64° at 13 mm.	(7)		

[For prepn. of $\bar{C}$ from fumaric acid (1:0895) with PCl_5 (1) (2) (3), with $SOCl_2$ (8) (10) (cf. (9) (11)), with phthalyl dichloride (3:6900) (12) (9) (10), or with benzotrichloride (3:6540) at 170° (27) see indic. refs.; from maleic anhydride (1:0625) by htg. 2 hrs. at

130–135° with phthaloyl dichloride (3:6900) + $ZnCl_2$ (82–95% yield (7)) or with PCl_5 (13) (6)· for formn. of C̄ from succinyl dichloride (3:6200) with Cl_2 see (14), from calcium malate with PCl_5 see (15).]

C̄ on htg. with fumaric acid (1:0895) at 175° (9) (16) or with silver fumarate (13) is largely converted to maleic anhydride (1:0625), b.p. 197–199°, m.p. 52°.

C̄ with Cl_2 in CCl_4 in sunlight adds halogen almost quant. (19) yielding (17) (18) (20) *meso*-α,α′-dichlorosuccinyl dichloride (3:9087). — C̄ adds Br_2 at 150° (2) or in CCl_4 in sunlight (20) yielding alm. quant. (19) *meso*-α,α′-dibromosuccinyl dichloride, b.p. 113° at 18 mm. (20) (this prod. hydrolyzes with aq. to *meso*-α,α′-dibromosuccinic acid, m.p. 257–258° in s.t. (20).

[C̄ with 1,4-diphenylbutadiene-1,3 yields (10) 3,6-diphenyltetrahydrophthaloyl dichloride, colorless ndls from lgr., m.p 143–144° cor. (10), this prod. on long boilg. (7½ hrs.) with aq. alc. NaOH gives (10) on acidif. 3,6-diphenyltetrahydrophthalic acid, ndls. from AcOH, m.p. 230–231° cor. dec. (10).] — [For color reactns. of C̄ with various polyenes see (21).]

[C̄ on htg. at 100° with $AlCl_3$ is partially conv. to maleyl dichloride accompanied by evolution of HCl + CO (22). — C̄ with $AlCl_3$ + C_6H_6 gives (yield: 78–83% (23), 74% (24)) *trans*-α,β-dibenzoylethylene (1,4-diphenybuten-2-dione-1,4), cryst. from C_6H_6 by addn. of alc., pale yel. ndls., m.p. 109–110° (23).] [For corresp. reactn. of C̄ + $AlCl_3$ with toluene (24) (25), chlorobenzene (24), mesitylene (24), anisole (24), *m*-xylene (25), and biphenyl (25) see indic. refs.]

C̄ with excess MeOH yields (8) dimethyl fumarate (1:2415), m.p. 101.7°. (Note, however, that C̄ with 1 equiv. MeOH in C_6H_6 stood 5 hrs. at room temp. (5) or in ether (26) yields fumaric methyl ester chloride, b p. 83° at 17 mm. (26), 76° at 22 mm. (5), m.p. 16° (5), this on shaking with aq. gives alm. quant. (5) methyl hydrogen fumarate, cryst. from C_6H_6, m.p. 144.5° cor (5).

C̄ with phenol (6) or with sodium phenolate in C_6H_6 (28) yields diphenyl fumarate, ndls. from alc., m.p 161–162° (6); note, however, that the half ester, phenyl hydrogen fumarate, has m.p. 130° (28).

C̄ with aq. readily hydrolyzes yielding fumaric acid (1:0895), m.p. abt. 293–295° subl.; for the diamide, dianilide, and other derivs. corresp. to C̄ see fumaric acid (1:0895).

3:5875 (1) Perkin, *J. Chem. Soc.* **53**, 575 (1888). (2) Kekulé, *Ann. Suppl.* **2**, 86–87 (1862/63). (3) von Auwers, Schmidt, *Ber.* **46**, 480 (1913). (4) Wassermann, *Ann.* **488**, 225 (1931). (5) Lutz, *J. Am Chem Soc.* **52**, 3430 (1930). (6) Anschütz, Wirtz, *Ber.* **18**, 1947–1949 (1885). (7) Kyrides, *Org. Syntheses*, **20**, 51–54 (1940). (8) Meyer, *Monatsh* **22**, 421–422 (1901). (9) W. A. van Dorp, G. C. A. van Dorp, *Rec. trav. chim.* **25**, 96–99 (1906). (10) *Kuhn, Wagner-Jauregg, Ber* **63**, 2664, 2678–2679 (1930).

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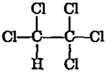
3:5880 PENTACHLOROETHANE ("Pentalin") C_2HCl_5 Beil. I - 87, I_1-(26), I_2-(57)



B.P.		
162.0°	at 760 mm.	(1)
161.95°	at 760 mm.	(2)
		(3) (24)
161.73°		(4)
161–162°		(5)
160.5°		(6)
159.1° cor.	at 760 mm.	(7)
159–160°		(8)
159–160°	at 753 mm.	(9)
159°		(10)
158.5–159.5°		(11)
158°	at 760 mm.	(12)
157.8°	at 734 mm.	(13)
152.2°	at 644 mm.	(13)
147.0°	at 563 mm.	(13)
149.8°	at 479 mm.	(13)
135.1°	at 406 mm.	(13)
128.2°	at 327 mm.	(13)
119.0°	at 247 mm.	(13)
108.2°	at 172 mm.	(13)
93.6°	at 103 mm.	(13)
69.0°	at 37 mm.	(13)

See also Note 1.

F.P.	
−29.5°	(14)
−29.0°	(1)
	(2) (15)
−22°	(16)

See also Note 2.

D_4^{25} = 1.67291 (1); 1.6712 (13)

n_D^{24} = 1.50250 (6); 1.501 (17)

D_4^{20} = 1.68052 (1) n_D^{20} = 1.50348 (80)

D_4^{15} = 1.68813 (1); 1.6846 (13) n_D^{15} = 1.50542 (1)

Note 1. For additional data on vapor press. of $\bar{C}$ at 5° intervals from 15–165° see (18).

Note 2. For effect of press. on f.p. of $\bar{C}$ see (15).

Colorless liquid with odor suggesting chloroform. — $\bar{C}$ is widely used in industry as solvent, degreasing agent, dry cleaner, component of insecticides, etc. — Note that comml. $\bar{C}$ is likely to contain other prods., notably tetrachloroethylene (3:5460) q.v.

$\bar{C}$ is very spar. sol. aq.; e.g., 1 g. $\bar{C}$ requires for soln. at 25° 2900 g. aq. (19): for study of soly. of $\bar{C}$ in aq. at 20° see (20); for study of soly. of aq. in $\bar{C}$ at 0°, 25°, and 30° as detd. by Karl Fischer reagt. see (21).

Binary systems contg. $\bar{C}$. For f.p./compn. data on systems $\bar{C}$ + *1,2-dichloroethane (ethylene dichloride)* (3:5130), eutectic, f.p. −62°, contg. about 56 wt. % $\bar{C}$ (22); $\bar{C}$ + *1,1,1-trichloroethane (methylchloroform)* (3:5085), eutectic, f.p. −69.0° contg. 72.3% $\bar{C}$ (14); $\bar{C}$ + *1,1,2,2-tetrachloroethane (acetylene tetrachloride)* (3:5750), eutectic, f.p. −73°, contg. 59.9 wt. % $\bar{C}$ (22); $\bar{C}$ + *tetrachloroethylene* (3:5460), eutectic, f.p. −54.8°, contg. 41.6% $\bar{C}$ (14); $\bar{C}$ + CCl_4 (3:5100), eutectic, f.p. −68° (82), $\bar{C}$ + CBr_4 (82) see indic. refs.

$\bar{C}$ forms binary azeotropes with various org. cpds.; e.g., $\bar{C}$ with chloroacetic acid (3:1370) forms a const.-boilg. mixt., b.p. 158.65° at 760 mm., contg. 90.1 wt. % $\bar{C}$ (23); $\bar{C}$ with trichloroacetic acid (3:1150) forms a const.-boilg. mixt., b.p. 161.8° at 760 mm., contg. 96.5 wt. % $\bar{C}$ (24). — For other examples see Beil. I_2-(57).

$\bar{C}$ either as liquid or vapor is extremely toxic; for further details see (83) (25) (26) (27) (28) (29); for extensive study of anthelmintic action see (19).

[For study of soly. in $\bar{C}$ of gaseous HCl (30) (11), H_2S (30), or NH_3 (30) see indic. refs.; for study of thermal conductivity of $\bar{C}$ see (31); for study of influence of vapors of $\bar{C}$ on

the explosion limits of mixtures of air with hydrogen, carbon monoxide, methane, acetylene, etc., see (32) (33) (34) (35).]

Preparation of $\bar{C}$. [For prepn. of $\bar{C}$ from chloral (3:5210) with PCl_5 (7) (37) or with $AlCl_3$ (38) see indic. refs.; note that in latter case (38) presence of $AlCl_3$ also facilitates loss of HCl from $\bar{C}$ with consequent formn. of tetrachloroethylene (3:5460); from trichloroethylene (3:5170) by addn. of Cl_2 in aq. (39) or under influence of ultra-violet light (40) (41) (note that O_2 retards addition of halogen (41)), or with S_2Cl_2 in s.t. at 140–150° (42), see indic. refs.]

[For formn. of $\bar{C}$ (together with various other by-products) from ethyl chloride (3:7015) (43) or from 1,2-dichloroethane (ethylene dichloride) (3:5130) (44) with Cl_2 see indic. refs.; from chloroform (3:5050) in electric arc (45) or in dark electric discharge (46) see indic. refs.; from CCl_4 in dark elec. discharge see (46); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) or from trichloroethylene (3:5170) with Cl_2 at 80°, 95°, or 115° in ultra-violet light (41), over pumice at 700° (47), or with $FeCl_3$ on htg. in s.t. (48) see indic. refs.; from trichloroethylene (3:5170) with large excess Cl_2O in CCl_4 at −20° see (10); from β,β'-dichlorodiethyl sulfide ("mustard gas") with dry Cl_2 at 100° see (49).]

[For stabilization of $\bar{C}$ by addn. of not over 0.1% alkyl amines such as Et_3N (50) or with a wide variety of other org. N cpds. (81) see indic. refs.]

[For studies of detn. of $\bar{C}$ by reactn. with Na + ethanolamine in dioxane (51) followed by volumetric (51) or gravimetric (71) detn. of resultant chloride ion see indic. refs. (note that use of Stepanov's method (Na + EtOH) for detn. of Cl in $\bar{C}$ gives low results unless after addn. of Na mixt. is refluxed at least 20 hrs. (12)); for detn. of $\bar{C}$ by thermal decn. and subsequent detn. of chlorine see (52).]

Chemical behavior of $\bar{C}$. [$\bar{C}$ with dry Cl_2 at 70° in diffuse light does not react and even after 30 hrs. no HCl is formed (52); however, $\bar{C}$ with dry Cl_2 + $AlCl_3$ at 70° (53), or $\bar{C}$ + Cl_2 over activated charcoal at 300–400° (54), yields hexachloroethane (3:4835).]

[$\bar{C}$ with F_2 at 90° over a 10-hr. period yields (8) a mixt. of prods. contg. fluoropentachloroethane, m.p. 99.8–110° (in s.t.) (b.p. 137–139°), hexachloroethane (3:4835), tetrachloroethylene (3:5460), *sym.*-difluorotetrachloroethane, b.p. 91–92°, together with other materials. — For behavior of $\bar{C}$ with SbF_3 see (55).]

$\bar{C}$ with $K_2Cr_2O_7/H_2SO_4$ is only partially oxidized to CO_2 (56). — [$\bar{C}$ on photochem. oxidn. with O_2 in ultra-violet light (57) (58) gives a mixt. consisting of 80% trichloroacetyl chloride (3:5420) + 20% phosgene (3:5000). — $\bar{C}$ with fumg. H_2SO_4 (60% SO_3) at 50–60° yields (59) dichloroacetyl chloride (3:5290).]

$\bar{C}$ under various circumstances loses HCl yielding tetrachloroethylene (3:5460) [e.g., $\bar{C}$ over bone char at 280° (60) or over $NiCl_2$ at 330° (61), or with $AlCl_3$ at 70° (53) or under reflux (95% yield (72)) (62), or with liq. NH_3 at −18 to −34° under reduced press. (63) (64), or with prim. or sec. aliph. amines (84), or with MeOH over Al_2O_3 at 290° (methyl chloride (3:7005) is also formed) (65), or with acetylene over cat. at 200–300° (vinyl chloride (3:7010) is also formed) (68), or with alc. KOH (44) (66), or in alc. with 2 *N* aqueous NaOH in cold (98% yield (12)) gives tetrachloroethylene (3:5460). — For detn. of $\bar{C}$ by titration of chloride ion thus split off see (67); for study of kinetics of reactn. of $\bar{C}$ with EtOH/NaOH see (12).]

$\bar{C}$ under certain conditions yields trichloroethylene (3:5170) [e.g., $\bar{C}$ with H_2 over Ni at 270° (61), or $\bar{C}$ on electrolysis at Pb cathode (69), or $\bar{C}$ with MeMgI (70) gives trichloroethylene (3:5170).]

[$\bar{C}$ with $CHCl_3$ (3:5050) + $AlCl_3$ gives (72) (73) (74) (75) *unsym.*-heptachloropropane (3:0200); note that this reactn. first involves loss of HCl under influence of $AlCl_3$ (see also above) and subsequent condensation of the resultant tetrachloroethylene (3:5460)

with $CHCl_3$. — C̄ (1 mole) + 1,2-dichloroethylene (presumably mixt. of *cis* (3:5042) and *trans* (3:5028) stereoisomers) + $AlCl_3$ (1% of sum of wts. of reactants) stood 12 days at 40° gives (76) (in addition to a residue a fraction volatile with steam which consists of 1,1,2,2,3,4,4-heptachlorobutane (3:9056)), two stereoisomeric 1,1,2,3,4-pentachlorobutanes, viz., the solid isomer (3:0750) and the liquid isomer (3:9068); for genesis of these compds. see (76).]

[For survey of actn. of C̄ on various common metals see (77). — C̄ with Na or K or their alloys may (like many other polychloro compds.) explode under certain conditions; for an extensive study of this behavior including sensitivity to mechanical shock see (78).]

C̄ with excess phenylhydrazine on stdg. at ord. temp. evolves N_2, ppts. phenylhydrazine hydrochloride, and yields benzene (67); the full mechanism of this behavior seems never to have been established, but these same three prods. are similarly obtd. from hexachloroethane (3:4835) and to a lesser degree from 1,1,2,2-tetrachloroethane (3:5750).

Ⓟ *Color test with NH_4OH/Cu_2Cl_2.* C̄ *(1–2 drops) in small glass-stoppered bottle* filled with conc. aq. NH_4OH treated with powdered Cu_2Cl_2, stopper quickly inserted (to force out air and excess liq.) and shaken, gives within 5 mins. a blue color which rapidly darkens; note that this test is not specific for C̄ and is also shown by other cpds. contg. the $—CCl_3$ group such as trichloroacetic acid (3:1150), ethyl trichloroacetate (3:5950) $CHCl_3$ (3:5050), CCl_4 (3:5100), although hexachloroethane (3:4835) develops color at surface only after several hours; for further details see (79).

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(31) Bates, Hazzard, Palmer, *Ind. Eng. Chem.* 33, 375–376 (1941). (32) Langen van der Valk, *Rec. trav. chim.* 48, 201–210 (1929). (33) Jorissen, *Ind. Eng. Chem.* 19, 430–431 (1927). (34) Coward, Jones, *Ind. Eng. Chem.* 18, 970–974 (1926). (35) Jorissen, Meuwissen, *Rec. trav. chim.* 44, 132–140 (1925). (36) Jorissen, Velisek, *Rec. trav. chim.* 43, 80–86 (1924). (37) Paterno, *Ann.* 151, 116–121 (1869). (38) Mouneyrat, *Bull. soc. chim.* (3) 19, 260–261 (1898). (39) Groll, Hearne (to N. V. de Bataafsche Petroleum Maatschappij), Brit. 436,357, Nov. 7, 1935; French 789,290, Nov. 25, 1935; *Cent.* 1936, [illegible] furt und Theilnehmer, Ger. 248,982, July [illegible]

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(51) Winteringham, *J. Soc. Chem. Ind.* **61**, 186–187 (1942); *C.A.* **37**, 1951 (1943). (52) Winteringham, *J. Soc. Chem. Ind.* **61**, 190–192 (1942), *C.A.* **37**, 1951 (1943). (53) Mouneyrat, *Bull. soc. chim.* (3) **17**, 797–799 (1897); (3) **19**, 182–183 (1898). (54) Mkryan, Babayan, *Sbornik Trudov. Armyanskogo Filiala Akad. Nauk* **1940**, No. 2, 51–58; *C.A.* **37**, 5694 (1943). (55) Henne, Ladd, *J. Am. Chem. Soc.* **58**, 402–403 (1936). (56) Guyot, Simon, *Compt. rend* **170**, 736 (1920). (57) Schumacher, Thürauf, *Z. physik. Chem.* **A-189**, 183–199 (1941); *Cent.* **1942**, I 1485; *C.A.* **36**, 4418 (1942). (58) Müller, Ehrmann, *Ber.* **69**, 2207–2210 (1936). (59) Chem. Fabrik. Weiler-ter-Meer, Ger. 362,748, Oct. 31, 1922; *Cent.* **1923**, II 405. (60) Körner, Suchy (to Dr. A. Wacker Soc. Chem. Ind.), Ger. 464,320, Aug 21, 1928, *Cent.* **1929**, I 1044.

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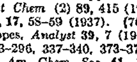
3:5885 1,2,3-TRICHLORO-2-METHYLPROPANE $C_4H_7Cl_3$ Beil. S.N. 10



;

B.P. 162.0–163.1° cor. (1) D_4^{25} **= 1.3020 (1)** n_D^{20} **= 1.4765 (1)**

[For prepn. of $\bar{C}$ from *ter*-butyl chloride (3.7045) + Cl_2 see (1); *for formn. of* $\bar{C}$ *(5%)* from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) by addn. of Cl_2 with Cl_2/aq. at 30° (main prod. is 1,3-dichloropropanol-2 (3:5985) in 70% yield) (2), or better with SO_2Cl_2 (83% yield (4)) see indic. refs.; from 1,3-dichloro-2-methylpropane (3:7960) with Cl_2, or with $SO_2Cl_2 + Bz_2O_2$ (73% yield) see (4).]

$\bar{C}$ on pyrolysis at 450–550° gives (3) three isomeric dichloroisobutenes, viz., *cis* and *trans* 1,3-dichloro-2-methylpropene (3:5590) and 3-chloro-2-(chloromethyl)propene-1 (3:5633).

[$\bar{C}$ on dehydrohalogenation with equimolal proportion of quinoline at b.p. 1½ hrs. gives (73–83% yield (4)) 1,3-dichloro-2-methylpropene-1 (3.5590).]

$\bar{C}$ on hydrolysis with excess 5% aq. NaOH gives (84% *yield* (3)) a mixt. of *cis* and *trans* stereoisomers of γ-chloro-β-methyl-allyl alcohol (3:8340).

3:5885 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1027–1029 (1936). (2) Burgin, Hearne, Rust, *Ind. Eng. Chem.* **33**, 387 (1941). (3) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1029–1031 (1936). (4) Mooradian, Cloke, *J. Am. Chem. Soc.* **68**, 787 (1946).

3:5890 ISOPROPYL DICHLOROACETATE $C_5H_8O_2Cl_2$ B

$(CH_3)_2CH.O.CO.CHCl_2$

B.P. 163.8–164.8° (1) $D_4^{25} = 1.1989$ (2) $n_D^{25} =$

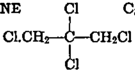
164.0° at 747 mm. (2) $D_4^{20} = 1.2053$ (3) $n_D^{20} =$

[For prepn. (48.6% yield (2)) from isopropyl alc. (1:6135) + dichloroacetic ac see (2); for prepn. (39.5% yield (2)) from propylene and dichloroacetic ac. (3: (2).]

[For study of hydrolysis of $\bar{C}$ see (3).]

3:5890 (1) Cheng, *Z. physik. Chem.* B-24, 310 (1934). (2) Dorris, Sowa, Nieuwland *Chem. Soc.* 56, 2689–2790 (1934). (3) Schjanberg, *Z. physik. Chem.* A-172, 229 (1935).

3:5895 1,2,2,3-TETRACHLOROPROPANE $C_3H_4Cl_4$ Beil. I I



B.P. 164° (1) $D_{17}^{17} = 1.496$ (1)

Colorless liq. with characteristic penetrating ethereal odor. — Insol. in aq.; ea alc., ether.

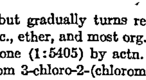
[For prepn. of $\bar{C}$ from 2,3-dichloropropene-1 (3:5190) with Cl_2 see (1); from 1,2, chloropropane (3:5475) with $SbCl_5$ at 100° see (2).]

$\bar{C}$ with alc. KOH splits out HCl yielding (1) 1,2,3-trichloropropene-1 (3:5650), b.p.

3:5895 (1) Pfeffer, Fittig, *Ann.* 135, 360–361 (1865). (2) Herzfelder, *Ber.* 26, 2436 (1893).

3:5900 1,3-DICHLOROBUTANONE-2 $C_4H_6OCl_2$ Beil. I - 67 I_1-(34 I_2—

(α-Chloroethyl chloromethyl ketone)



B.P. 165° (2) at 753 mm. (1) $D_4^{20} = 1.3116$ (3) $n_D^{20} = 1.4686$ (

65° at 17 mm. (2) $D_4^{15} = 1.3189$ (3) $n_D^{15} = 1.4702$ (

60° at 13 mm. (2)

55–55.5° at 10 mm. (3)

Colorless liq. when freshly distd. but gradually turns red. — Strong lachrymator and nasal irritant (1). — Insol. aq.; sol. alc., ether, and most org. solvents.

[For prepn. from ethyl methyl ketone (1:5405) by actn. of Cl_2 (1), from 1,3-dichlorobutanol-2 (3:9145) by oxidn. (3); from 3-chloro-2-(chloromethyl)butene-1 (3:9206) with O_3 (4) see indic. refs.]

$\bar{C}$ with satd. aq. $NaHSO_3$ soln. yields cryst. $NaHSO_3$ cpd. (1). — $\bar{C}$ with Zn dust + AcOH yields (1) (3) ethyl methyl ketone (1:5405).

Ⓓ 1,3-Dichlorobutanone-2 semicarbazone: m.p. 114° (2), 107–108° (4).

3:5900 (1) Démètre-Vladesco, *Bull. soc. chim.* (3) 6, 829–830 (1891). (2) Blaisé, *Bull. soc. chim.* (4) 15, 733 (1914); *Compt. rend.* 156, 794 (1913). (3) Petrov, *J. Gen. Chem.* (*U.S.S.R.*) 11, 713–721 (1941); *C.A.* 36, 404 (1941). (4) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) 8, 1232–1246 (1938); *Cent.* 1939, II 4223; [*C.A.* 33, 4190 (1939)].

3:5910 α,α,β-TRICHLORO-*n*-BUTYRALDEHYDE ("Butyrchloral"; "Butylchloral"; Crotonchloral) $C_4H_5OCl_3$ Beil. I - 664 I_1-(346) I_2-(725)

```
          Cl
          |
CH3.CH.C.CHO
    |   |
    Cl  Cl
```

B.P.

164.5–165.5° at 760 mm. (1)		$D_4^{20} = 1.3956$ (4)	$n_D^{20} = 1.47554$ (4)
165°	(2)		
164–165° at 750 mm.	(3) (4)	$D_{15}^{18.8} = 1.4237$ (5)	
163–164°	(6)		

[*See also* "*Butyrchloral hydrate*" (3:1905).]

Oily liq.

[For prepn. of $\bar{C}$ from acetaldehyde (1:0100) (3) (7) or paraldehyde (1:0170) (7) (8) with Cl_2 see indic. refs.; from α-chlorocrotonaldehyde (3:8117) by addn. of Cl_2 (6) (10) (36) in CCl_4 soln. (9); from crotonaldehyde (1:0150) by satn. with HCl gas followed by treatment with Cl_2 see (11) cf. (37).]

[For prepn. of $\bar{C}$ from its polymers (see below) by distn. at atmospheric press. (2), or from its hydrate (3:1905) by distn. with half its wt. of Ac_2O (2), or shaking with conc. H_2SO_4 (1) cf. (2), see indic. refs.]

[$\bar{C}$ on reduction with fused $Al(OEt)_3$ in boilg. abs. alc. under H_2 or N_2 for 14 hrs. (12) or with fused $Al(OEt)_3 + AlCl_3$ in boilg. abs. alc. under H_2 or N_2 for 14 hrs. (13), or with C_2H_5OMgBr in dry ether followed by aq. (19), or by treatment with diethylzinc (14), di-*n*-propylzinc (15), or di-isobutylzinc (15) (followed by aq.) gives (92% yield (12)) 2,2,3-trichlorobutanol-1 (3:1336), m.p. 62°. — Note that $\bar{C}$ (as hydrate) (3:1905) is reduced by fermenting yeast (16) to dextrorotatory 2,2,3-trichlorobutanol-1, m.p. 62°.]

[$\bar{C}$ with Zn + HCl or Zn + aq. (17) is dehalogenated to a mixt. of α-chlorocrotonaldehyde (3:8117) + crotonaldehyde (1:0150); $\bar{C}$ with Fe filings + AcOH at room temp. for 8 days (18) dehalogenates to a mixt. of *n*-butyraldehyde (1.0130) + *n*-butyl alc. (1:6180) + crotonyl alc. [Beil. I-442, I_1-(227), I_2-(480)].]

$\bar{C}$ on oxidn. with 2 pts. fumg. HNO_3 stood overnight at ord. temp. yields (3) α,α,β-trichloro-*n*-butyric acid (3:1280) (cf. corresp. behavior of butyrchloral hydrate (3:1905)). — $\bar{C}$ on oxidn. with boilg. aq. $K_4Fe(CN)_6$ also loses 2 atoms of chlorine giving (41% yield (29)) α-chlorocrotonic acid (3:2760).

$\bar{C}$ (1 mole) with H_2O (1 mole) readily combines with evolution of heat yielding (3) (9) crystn. butyrchloral hydrate (3:1905). — Similarly, $\bar{C}$ combines with equiv. amt. of alcohols giving the corresp. alcoholates: e.g., $\bar{C}$ with EtOH yields (20) butyrchloral-ethylalcoholate [Beil. I-665, I_1-(346)]; $\bar{C}$ with butanol-2 yields (1) butyrchloral-*sec*-butylalcoholate, etc. — Note that butyrchloral-ethylalcoholate in excess EtOH on satn. with dry HCl gas gives (50% yield (21)) α,α,β-trichloro-*n*-butyraldehyde diethylacetal, b.p. 232–233°, 135° at 30 mm. (21). — [For study of dissociation of addn. cpds. of $\bar{C}$ with various *prim.*, *sec.*, and *ter.* alcohols see (22).]

$\bar{C}$ or its hydrate (3:1905) q.v. in pres. of conc. H_2SO_4 or pyridine at ord. temp. can be trimerized to a mixt. of two parabutyrchlorals (2); these are colorless, crystalline, sharp melting solids, sol. in org. solvents but insol. in aq.; the less sol. α-parabutyrchloral, rhombic cryst. from boilg. AcOH or boilg. EtOH, has m.p. 180°; the more soluble β-parabutyrchloral (stereoisomer?), cryst. from boilg. AcOH or boilg. EtOH, has m.p. 157°; these polymers can be distilled at 15 mm., but attempts to distil them at ord. press. result in complete dissociation to $\bar{C}$ (2).

[$\bar{C}$·with anhydrous acetaldehyde (1:0100) (2 moles) with dry HCl gas at 0° for 15–20 hrs. condenses to give (67% yield (23)) 2,4-dimethyl-6-(α,α,β-trichloro-n-propyl)trioxane-1,3,5, b.p. 118° at 13 mm. (23).]

[$\bar{C}$ in $CHCl_3$ with H_2S gives (24) *bis*-(α-hydroxy-β,β,γ-trichloro-n-butyl)sulfide ("butyrchloralsulfhydrate"), m.p. 85° (24).]

[$\bar{C}$ with PCl_5 (1.4 wt. pts.) at 110–120° apparently has its oxygen replaced by equivalent chlorine but also loses 1 HCl yielding (25) a cpd. of compn. $C_4H_2Cl_4$, presumably 1,1,2,3-tetrachlorobutene-2, although no other report of this cpd. can be found.]

[$\bar{C}$ with aq. HCN gives only butyrchloral hydrate (3:1905) since this prod. is too spar. sol. aq. to enter further reaction, but upon addn. of alc. and subsequent digestion this system yields (26) (27) α,α,β-trichloro-n-butyraldehyde cyanohydrin [Beil. III-322, III_1-(226)], pl. from aq , m.p. 101–102° (27) (28), also obtd. from butyrchloral hydrate with aq. KCN (2 moles) at 40° (28). — See also further comments under butyrchloral hydrate (3:1905).]

[$\bar{C}$ with ethyl diazoacetate gives (71% yield (30)) ethyl β-keto-γ,γ-trichloro-n-caproate [Beil. III-684], b.p. 149° at 20 mm. (30).]

$\bar{C}$ in $CHCl_3$ with NH_3 gas gives on evapn. of solvent (31) butyrchloralammonia, cryst., m.p. 62° [see also under butyrchloral hydrate (3:1905)].

$\bar{C}$ also readily adds amides yielding cpds. of type $CH_3.CHCl.CH_2CH(OH).NH.CO.R$; e.g., $\bar{C}$ with acetamide (1 mole) gives on htg. (31) (32) (33) (34) butyrchloralacetamide, obtd. by these workers in two isomeric forms one of m.p. 170° (spar. sol. hot alc.) (32) (33) (34), the other m.p. 158° (readily sol. in hot 50% alc.) (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with acetamide (1 mole) htd. at 100° until solidification occurs gives only (21) a prod. m.p. 208–210°; $\bar{C}$ with benzamide (1 mole) gives on htg. butyrchloralbenzamide, obtd. in two isomeric forms, one of m.p. 146° (32) (33) cf. (34), the other of m.p. 132° (31) (32) (33); note, however, that butyrchloral hydrate (3:1905) with benzamide yields only (21) a prod. m.p. 176°.

$\bar{C}$ (3.5 g.) with urea (1.2 g.) htd. at 100°, cooled, powdered and recrystd. from alc., gives (yield not stated (35)) butyrchloralurea, m.p. 156°.

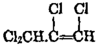
3:5910 (1) Willcox, Brunel, *J. Am. Chem. Soc.* **38**, 1837 (1916). (2) Chattaway, Kellett, *J. Chem. Soc.* **1928**, 2709–2714. (3) Krämer, Pinner, *Ber.* **3**, 383–390 (1870). (4) Brühl, *Ann.* **203**, 20 (1880). (5) Dobrosserdow, *Cent.* **1911**, I 955. (6) Pinner, *Ber.* **8**, 1564–1566 (1875). (7) Pinner, *Ann.* **179**, 24–30 (1875). (8) Freundler, *Bull. soc. chim.* (4) **1**, 68–69 (1907). (9) *Moureu, Murat, Tampier, Bull. soc. chim. (4)* **29**, *33 (1921).* (10) Lieben, Zeisel, *Monatsh.* **4**, 533–536 (1883).

(11) High (to Udylite Corp.), U.S. 2,280,290, April 21, 1942; *C.A.* **36**, 5482 (1942). (12) Meerwein, Schmidt, *Ann.* **444**, 233–234 (1925). (13) Meerwein (to F. Bayer & Co.), U.S. 1,572,742, Feb. 9, 1926; *Cent.* **1926**, I 3627: Brit. 251,890, June 3, 1926; *Cent.* **1926**, II 1097. (14) Garzarolli-Thurnlackh, *Ann.* **213**, 369–372 (1882). (15) Garzarolli-Thurnlackh, Papper, *Ann.* **223**, 166–169 (1884). (16) Rosenfeld, *Biochem. Z.* **156**, 54–57 (1925); *Cent.* **1925**, I 2301; *C.A.* **19**, 2683 (1925). (17) Sarnow, *Ann.* **164**, 108 (1872). (18) Lieben, Zeisel, *Monatsh.* **1**, 840–843 (1880). (19) I.G., Brit. 384,156, Dec. 22, 1932; *Cent.* **1933**, I 1351. (20) Pinner, *Ann.* **179**, 38–42 (1875).

(21) Freundler, *Bull. soc. chim.* (4) **1**, 201, 203–204 (1907); *Compt. rend* **143**, 684 (1906). (22) Willcox, Brunel, *J. Am. Chem. Soc.* **38**, 2533–2535 (1916). (23) Helferich, Besler, *Ber.* **57**, 1277, 1279–1280 (1924). (24) Voswinkel, Ger. 233,857, April 24, 1911; *Cent.* **1911**, I 1467. (25) Judson, *Ber.* **3**, 790 (1870). (26) Pinner, Bischoff, *Ann.* **179**, 97–99 (1875). (27) Pinner, Klein, *Ber.* **11**, 1488 (1878). (28) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1043–1046. (29) Wallach, *Ber.* **10**, 1530 (1877). (30) Schlotterbeck, *Ber.* **42**, 2572 (1909).

(31) Schiff, Tassinari, *Ber.* **10**, 1784–1786 (1877). (32) Schiff, *Ber.* **25**, 1690–1691 (1892). (33) Tarugi, *Gazz. chim. ital.* **24**, I 230–236 (1894). (34) Pinner, *Ann.* **179**, 39–40 (1875). (35) Feist, Kublinski, *Arch. Pharm.* **274**, 430, 434 (1936). (36) Chem. Fabrik vorm. Weiler ter-Meer, Ger. 351,137, April 3, 1922; *Cent.* **1922**, IV 155. (37) Brown, Plump (to Pennsylvania Salt Mfg. Co.), U.S. 2,351,000, June 13, 1944; *C.A.* **38**, 5226 (1944).

3:5920 1,2,3,3-TETRACHLOROPROPENE-1 $C_3H_2Cl_4$ Beil. I — I_1-(83) I_2—



B.P. 165° (1)
165–167° (2)

D_4^{34} = 1.5274 (1) **n_D^{13} = 1.5272 (1)**

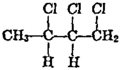
Colorless oil.

[For prepn. (70% yield (2)) from *sym.*-pentachloropropane (3:6280) by actn. of alc. KOH (1 mole) see (2).]

C̄ with conc. H_2SO_4 at 30–40° gives quant. yield of chloromalondialdehyde [Beil. I-765].

3:5920 (1) Prins, *J. prakt. Chem.* (2) 89, 421–422 (1914). (2) Heilbron, Heslop, Irving, *J. Chem. Soc.* 1936, 783.

3:5935 1,2,3-TRICHLOROBUTANE $C_4H_7Cl_3$ Beil. I - 119 I_1— I_2-(82)



B.P. 165–167° at 759 mm. (1)
165–168° at 725 mm. (2)
79–80° at 32 mm. (3)
62–63° at 28 mm. (2)

D_4^{20} = 1.3164 (1) **n_D^{20} = 1.4790 (1)**
D_4^{18} = 1.3172 (1)
D_0^{0} = 1.3241 (3)

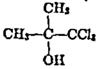
Insol. aq., sol. alc., ether, $CHCl_3$.

[For formn. of C̄ (36.5%) from 2,3-dichlorobutane (3:7615) + sl. excess Cl_2 in dark at −17° (together with 18% 2,2,3-trichlorobutane (3:5680)) see (1); for formn. of C̄ (19%) from 1,2-dichlorobutane (3:7680) + sl. excess Cl_2 in dark at −17° (together with 28% 2,2,3-trichlorobutane (3:5680) see (1); for formn. of C̄ from 1-chlorobutene-2 (3:7205) + Cl_2 in $CHCl_3$ see (3); for formn. of C̄ from butene-1 with Cl_2/aq. (together with 1,2-dichlorobutane (3:7680)) see (2).]

C̄ with solid KOH at 150° loses HCl yielding (1) mixt. of *cis*-1,2-dichlorobutene-2 (3:5615), b.p 125–127°), and *trans*-1,2-dichlorobutene-2 (3:5360), b.p. 116–118° at 765 mm. (1).

3:5935 (1) Tishchenko, Churbakov, *J. Gen. Chem.* (*U.S.S.R.*) 6, 1553–1558 (1936); *C.A.* 31, 2165 (1937), *Cent.* 1937, I 3786. (2) de Montmollin, Matile, *Helv. Chim Acta* 7, 108 (1924). (3) Charon, *Ann. chim* (7) 17, 230–231 (1899).

—— 1,1,1-TRICHLORO-2-METHYLPROPANOL-2 $C_4H_7OCl_3$ Beil. I - 382 I_1-(192) I_2-(415)



B.P. 167° **M.P. 96–97°**

See 3:2662. *Division A: Solids.*

3:5950 ETHYL TRICHLOROACETATE $C_4H_5O_2Cl_3$ Beil. II - 209

$Cl_3C.COOC_2H_5$ II_1-(94) II_2-(200)

B.P. 167.5–168.0° cor.	(1)	D_4^{20} = 1.3826 (8)	n_D^{20} = 1.45068 (8)
167.5°	(2)	1.3823 (10)	1.45046 (10)
166.7–167.1° at 754.8 mm.	(3)		
167°	(4)		
166°	(13)		
166° at 738.2 mm.	(8)		
164–166°	(5)		
164°	(6)		
163.0–163.5° at 682 mm.	(7)		
74° at 28 mm.	(9)		
58.0–59.0° at 13 mm.	(10)		
62° at 12 mm.	(11)		
60–61° at 12 mm.	(12)		

[For prepn. of C̄ from trichloroacetic acid (3:1150) with abs. EtOH + dry HCl (yield: 90% (13), 53% (16)) or with H_2SO_4 (50–60% yield (13)) (14) (15), or with Twitchell's reagt. (62.6% yield (5)) see indic. refs.; from trichloroacetyl chloride (3:5420) with ethyl orthoformate (1:3241) see (17); from "tetrachloroethylidene trichlorolactate" [Beil. XIX-105] with EtOH see (12); for formn. of C̄ from chloral (3:5210) with $Al(OEt)_3$ in C_6H_6 (11), or with acetaldehyde + $Al(OEt)_3$ or $Mg(OMe)_2$ in dry ether (18), see indic. refs.]

[C̄ on warming with KCN in abs. alc. dec. (6) into chloroform (3:5050) + CO_2; C̄ with NaOEt gives on warming (19) triethyl orthoformate (1:3241) + Na ethyl carbonate + NaCl.]

[C̄ with excess H_2 over Ni at 320° gives (14) ethyl dichloroacetate (3:5850) + ethyl chloroacetate (3:5700) + EtOAc (1:3015) + acetaldehyde (1:0100).]

C̄ with Cu_2Cl_2 in conc. aq. NH_4OH gives dark blue color within 2 min. (21); also shown by chloral hydrate (3:1270) and trichloroacetic acid (3:1150) (the latter, however, acting instantly); for further limitations see (21). [C̄ htd. at 100° with Cu powder for 6–8 hrs. (22) gives diethyl tetrachlorosuccinate, b.p. 156° at 13 mm. (22).]

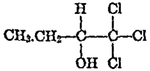
C̄ with conc. aq. NH_4OH gives in the cold (14) trichloroacetamide, spar. sol. aq., cryst. from hot aq. or dil. alc., m.p. 141°. — C̄ on shaking with aq. benzylamine gives in the cold (23) trichloroacet-*N*-benzylamide, cryst. from lgr., m.p. 93.6–94.4° cor. (23). [Note, however, that the corresp. dichloroacet-*N*-benzylamide (from ethyl dichloroacetate (3:5850) has almost the same m.p., viz., 94.8–95.6° cor. (23), while chloro-acet-*N*-benzylamide (from ethyl chloroacetate (3:5700)) has m.p. 93.0–93.6° cor. (23).]

C̄ hydrolyzes very readily (5) yielding ethyl alcohol (1:6130) and trichloroacetic acid (3:1150). [For kinetic studies of hydrolysis of C̄ under various conditions (including very high pressure (9)) see (10) (2) (24); for kinetic study of alcoholysis of C̄ with MeOH+ HCl see (25).]

3:5950 (1) Perkin, *J. Chem. Soc.* **65**, 423 (1894). (2) Timm, Hinshelwood, *J. Chem. Soc.* **1938**, 862–869. (3) Schiff, *Ann.* **220**, 108 (1883); *Z. physik. Chem.* **1**, 379 (1887). (4) Cheng, *Z. physik. Chem.* **B-24**, 306 (1934). (5) Zaganiaris, Varvoglos, *Ber.* **69**, 2280 (1936). (6) Claus, *Ann.* **191**, 58–63 (1878). (7) Sudborough, Karne, *J. Indian Inst. Sci.* **5**, 7 (1922); *Cent.* **1923**, I 295; *C.A.* **17**, 665 (1923). (8) Brühl, *Ann.* **203**, 22–23 (1880). (9) Newitt, Linstead, Sapiro, Boorman, *J. Chem. Soc.* **1937**, 876–883. (10) Palomaa, Salmi, Korte, *Ber.* **72**, 790–797 (1939).
(11) Dworzak, *Monatsh.* **47**, 11–15 (1926). (12) Anschütz, Haslam, *Ann.* **253**, 125 (1889). (13) L. Spiegel, P. Spiegel, *Ber.* **40**, 1734 (1907). (14) Clermont, *Compt. rend.* **133**, 737–738

(1901). (15) Dumas, *Ann.* 32, 112 (1839). (16) Toole, Sowa, *J. Am. Chem. Soc.* **59**, 1972 (1937). (17) Levaillant, *Compt rend.* **195**, 882 (1932). (18) Nakai, *Biochem. Z.* **152**, 269–273 (1924). ... Mailhe, *Compt. rend.* **169**, 760 (1919). ... -1131 (1919). (22) Doughty, Freeman, *J. Am.* ... Mackenzie, *J. Am. Chem. Soc.* **59**, 421–422 (1937). (25) Kolhatkar, *J. Chem. Soc.* **107**, 930 (1915).

3:5955 *d,l*-**1,1,1-TRICHLOROBUTANOL-2** (Ethyl-trichloromethyl-carbinol) $C_4H_7OCl_3$ Beil. I — I_1— I_2-(403)



B P. 169–171° at 738 mm. (1)
82–84° at 22 mm. (2)
69–71° at 12 mm. (3)
68–70° at 13 mm. (1)
44–46° at 3 mm. (1)

$D_{25}^{25} = 1.3760$ (1) $n_D^{25} = 1.4901$ (1)

Oil. — Eas. sol. MeOH, EtOH, ether, acetone, C_6H_6, $CHCl_3$, CCl_4, CS_2. [Note that b.p. of 99° at 680 mm. (4) may be a typographical error (1).]

[For prepn. of C̄ from chloral (3:5210) via conversion with diazomethane to 3,3,3-trichloro-1,2-epoxypropane (3.1336) and reactn. of latter with 1 *N* LiMe in dry ether at −75° (yield 85%) see (1); from chloral (3:5210) with EtMgBr (4) (5) or EtMgI (2) in ether (yields: 44% (4), 16% (2), 15% (5)) see indic. refs. (note, however, that by virtue of reducing actn. of EtMgX large amounts of 2,2,2-trichloroethanol-1 (3:5775) are also formed (5) (2) (1)); from chloral (3:5210) with $PbEt_4$ (20% yield (6)) (note, however, that this could not be confirmed (1)), from trichloroacetyl chloride (3:5420) with EtMgBr at 10° see (3).]

C̄ with conc. HCl + $ZnCl_2$ (Lucas' reagent) stood for 1 hr. at room temp. gives (1) 1,1,1,2-tetrachlorobutane (3:5622).

C̄ with 5% soln. of Na_2CO_3 in 50% aq. alc. refluxed for 10 hrs. (1) or C̄ with aq. KOH, NaOH, Na_2CO_3, $Ba(OH)_2$, $Mg(OH)_2$, $CaCO_3$, etc., (2) undergoes both hydrolysis and hydrolytic cleavage giving respectively α-hydroxy-*n*-butyric acid [Beil. III-302, III_1-(114), III_2-(216)] (yields: 46% (1), 21% (2)), m.p. 43°, and propionaldehyde (1:0110) (29% yield (2)).

—— **Ethyl-trichloromethyl-carbinyl acetate:** b.p. 164–165° at 680 mm. (4). [From C̄ with Ac_2O at 130–135° for 2 hrs. (4). Note that in light of subsequent work (1) the identity of this prod. has been questioned.]

—— **Ethyl-trimethyl-carbinyl benzoate:** b.p. 217–218° at 680 mm. (4). [From C̄ with BzCl + cold dil. aq. alk. (4). Note that in light of subsequent work (1) the identity of this prod. has been questioned]

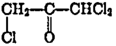
Ⓓ **Ethyl-trimethyl-carbinyl *p*-nitrobenzoate:** cryst. from pet. ether, m.p. 70–71.5° (1). [Note that this m.p. is identical with that of the *p*-nitrobenzoate of 2,2,2-trichloroethanol-1 (3:5775); although each appears to be authentic, whether their mixture shows depression of m.p. is not reported.]

3:5955 (1) Gilman, Abbott, *J. Org Chem.* **8**, 224–229 (1943). (2) Hébert, *Bull. soc. chim.* (4) **27**, 49, 55 (1920). (3) Jacob, *Bull. soc. chim* (5) **7**, 581–586 (1940); *C.A.* **36**, 3507 (1942). (4) Howard, *J. Am. Chem. Soc.* **48**, 774–775 (1926). (5) Iotsich, *J. Russ. Phys.-Chem. Soc.* **36**, 415 (1904); *Bull. soc. chim.* (3) **34**, 329 (1905). (6) Meerwein, Hinz, Majert, Sönke, *J. prakt. Chem* (2) **147**, 234, Note 1 (1936).

3:5957 1,1,3-TRICHLOROPROPANONE-2 $C_3H_3OCl_3$ Beil. I - 655

(α,α,γ-Trichloroacetone) I_1—

I_2—



B.P. 172° (1)

[For prepn. of Č from 1,1-dichloro-3-bromopropanone-2 (1) with alc. $HgCl_2$ see (1); for formn. from acetone (1:5400) with Cl_2 in pres. of $NiCl_2$ at 70° (together with other prods.) see (2).]

Č with aq. or alc. NH_4OH *fails* (1) to give chloroform; Č with KOH + aniline *fails* (1) to give phenylisocyanide. [Dif. from isomeric 1,1,1-trichloropropanone-2 (3:5620).]

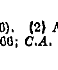
[Č with diazotized aniline in pres. of NaOAc couples (3) to yield a cpd. having composition $C_9H_7ON_2Cl_3$ (and presumably structure $C_6H_5.NH.N{=}C(Cl).CO.CHCl_2$), cryst from pet. ether, m.p. 115–116° (3).]

3:5957 (1) Cloëz, *Ann. chim.* (6) **9**, 170 (1886). (2) Akashi, *Bull. Inst. Phys.-Chem. Research (Tokyo)* **12**, 329–340 (1933); *Cent.* **1933**, I 3066; *C.A.* **27**, 3147 (1933). (3) Favrel, *Bull. soc. chim.* (5) **1**, 986–987, 989 (1934).

3:5960 *m*-DICHLOROBENZENE $C_6H_4Cl_2$ Beil. V - 202

V_1-(111)

V_2-(154)



B.P.		F.P.					
172.8°	(1)	−24°	(6)	$D_4^{20.0}$ = 1.2879	(11)	$n_D^{20.9}$ = 1.5470	(11)
172.0–172.6°	(2)	−24.1°	(12)				
172–173°	(7)	−24.2°	(12)	D_4^{20} = 1.2881	(8)		
172° cor. at 766 mm.	(3)	−24.4°	(8)	1.289	(11)		
172.1° at 742.4 mm.	(4)	−24.8°	(7)	1.287	(1)		
169–170° at 755 mm.	(5)	−25°	(5)			$n_D^{17.3}$ = 1.5472	(8)
170° cor. at 744 mm.	(6)	−26.25°	(9)			n_D^{17} = 1.5480	(7)
66° at 20 mm.	(7)		(10)	D_4^{15} = 1.2937	(8)		

Č when pure is colorless oil, volatile with steam.

[For f.p./compn. data and diagram of system Č + *o*-dichlorobenzene (3:6055) (eutectic, m.p. −45.9°, contg. 51.3% Č) see (12); on system Č + *p*-dichlorobenzene (3:0980) (eutectic, m.p. −29.9°, contg. 88.0% Č) see (12); for f.p./compn. data on ternary system of all three dichlorobenzenes see (7); for f.p./compn. data on systems: Č + fluorobenzene, Č + chlorobenzene (3:7903), Č + bromobenzene, and Č + *o*-chlorotoluene (3:8245) see (9).]

[For data on densities of solns. of Č in C_6H_6 (1:7400) and in *n*-hexane (1:8530) see (13).]

[Č is very spar. sol. aq. (for study of this over range 20–60° see (14)).]

[For prepn. of Č from *m*-chloroaniline [Beil. XII-602, XII_1-(300)] via diazotization and use of Cu_2Cl_2 reactn. (yields: 80% (15), 70% (16)) (7) (17) or by pptn. of the diazonium chloroplatinate and htg. of latter with Na_2CO_3 (4) see indic. refs.; from 2,4-dichloroaniline [Beil. XII-621, XII_1-(309)] via diazotization in alc. (18) (17) (3) (4) or isoamyl alc. (19) followed by replacement of orig. amino group by H by actn. of the alc. (60% yield (15)) or with hypophosphorous acid (50% yield (19)) (use of alk. $SnCl_2$ or oxidn. of the corresp. 2,4-dichlorophenylhydrazine with $CuSO_4$ gave only very low yields (15)) see indic. refs.; from *m*-phenylenediamine [Beil. XIII-33, $XIII_1$-(10)] via tetrazotization in AcOH with

nitrosylsulfuric acid followed by use of Cu_2Cl_2 reactn. (70.4% yield (20)) (21) see indic. refs.]

[For prepn. of $\bar{C}$ from *m*-chloronitrobenzene [Beil. V-243, V_1-(129)] with $SOCl_2$ in s.t. at 190–200° for 12 hrs. (71% yield (22)), from *m*-nitrobenzenesulfonic acid [Beil. XI-68, XI_1-(21)] with $SOCl_2$ in s.t. at 180–200° (23), from *m*-bromonitrobenzene [Beil. V-248, V_1-(131)] with PCl_5 in s.t. at 180° (24), from 2,6-dichlorobenzoic acid (3:4200) by htg. in acetamide at 225–235° for 6 hrs. (93% yield (25)), or from 2,6-dichlorobenzaldehyde (3:1690) with 50% KOH under N_2 at 100° for 5 hrs. (84% yield (6)) see indic. refs.]

[For formn. of $\bar{C}$ from 2,6-dichloroacetophenone (5), 2,4-dichlorobenzophenone (3:0825) (26), 2,6-dichlorobenzophenone (3:2285) (26), or 3,5-dichlorobenzophenone (3:1505) (26) by fusion with KOH/NaOH see indic. refs.; for formn. of $\bar{C}$ from 1,3-dichlorocyclohexadiene-1,3 [Beil. V-114] with PCl_5 or with Br_2 in $CHCl_3$ see (27).]

[For formn. of $\bar{C}$ from C_6H_6 (1:7400) or chlorobenzene (3:7903) with Cl_2 + cat. at 400–700° (50–60% yield (12)) (28) or with Cl_2 in pres. of $AlCl_3$ (29) cf. (30) see indic. refs.]

[$\bar{C}$ with Cl_2 + Al/Hg (31) or with Cl_2 + $AlCl_3$ (30) cf. (29) gives mainly 1,2,4-trichlorobenzene (3:6420). — $\bar{C}$ suspended in 1% aq. NaOH adds 3 Cl_2 in sunlight giving (32) *m*-dichlorobenzene hexachloride, cryst. from alc., m.p. 81.8° (32). — For study of photochemical chlorination of $\bar{C}$ see (33).]

[$\bar{C}$ with Mg (1 mole) + I_2 (0.25 equiv.) gave (34) after 3 days 62.5% *m*-chlorophenyl MgCl.]

[$\bar{C}$ with $CHCl_3$ + $AlCl_3$ at 65° for 14 hrs. as directed gives (18% yield (35)) *tris*-(2,4-dichlorophenyl)methane, white cryst. from hot acetone, m.p. 227–228.5° (35). — $\bar{C}$ with CCl_4 + $AlCl_3$ as directed gives (60% yield (35)) 2,4,2′,4′-tetrachlorobenzophenone dichloride, white pl. from hot acetone, m.p. 139.0–140.5° (35), 140° (36); hydrolysis of this prod. with $AcOH/H_2SO_4$ yields (37) 2,4,2′,4′-tetrachlorobenzophenone, m.p. 78° (37), accompanied by some 2,4-dichlorobenzoic acid (3:4560), m.p. 161° (37).]

[$\bar{C}$ with acetyl chloride (3:7065) + $AlCl_3$ gives (15% yield (38)) 2,4-dichloroacetophenone, b.p. 140–150° at 15 mm. (38), m.p. 33–34° (38). — $\bar{C}$ with chloroacetyl chloride (3:5235) + $AlCl_3$ in CS_2 yields (39) 2,4-dichlorophenacyl chloride (2,4,ω-trichloroacetophenone), pr. from lgr., m.p. 57° (39). — $\bar{C}$ with β-chloro-*n*-butyric acid (3:0035) + $AlCl_3$ or conc. H_2SO_4 yields (40) by condens. and subsequent ring closure 4,6-dichloro-3-methylindanone-1, m.p. 67–70° (40). — $\bar{C}$ with *o*-bromobenzoyl chloride + $AlCl_3$ in CS_2 gives (43% yield (41)) 2-bromo-2′,4′-dichlorobenzophenone, b.p. 227–228.5°, m.p. 33–34°.]

[$\bar{C}$ with phthalic anhydride + $AlCl_3$ at 100–110° for 7 hrs. gives (17% yield on the anhydride (42)) (43) *o*-(2,4-dichlorobenzoyl)benzoic acid, white cubes from C_6H_6 or $CHCl_3$, m.p. 106–107° (42), 100–101° (43), accompanied (44) (especially if acetylene tetrachloride is used as solvent) by 3,3-*bis*-(2′,4′-dichlorophenyl)phthalide, m.p. 176° (44); the above *o*-(2,4-dichlorobenzoyl)benzoic acid with fumg. H_2SO_4 at 155–160° ring-closes (90% yield (42)) to 1,3-dichloroanthraquinone [Beil. VII-787, VII_1-(411)], yel. ndls. from AcOH, m.p. 209–210° (42).]

[$\bar{C}$ on hydrolysis with steam + cat. at 550–850° yields (45) *m*-chlorophenol (3:0255) and/or resorcinol (1:1530). — For studies of reactn. of $\bar{C}$ with NaOMe/MeOH see (46) (47) (48).]

[$\bar{C}$ with conc. aq. NH_4OH in pres. of CuO under press. at 150–200° (49) cf. (50) (51) yields *m*-phenylenediamine. — $\bar{C}$ with K diphenylamine gives on htg. (16) (52) *N,N,N′,N′*-tetraphenyl-*m*-phenylenediamine [Beil. XIII-42], m.p. 137.5–138° (16) (52) (note that this same prod. is similarly obtd. from *o*-dichlorobenzene (3:6055) and in part also from *p*-dichlorobenzene (3:0980).]

[$\bar{C}$ on mononitration, e.g., by soln. in 4.5 moles HNO_3 (D = 1.5) in cold followed by 10 min. htg. at 70° (53) or with 5 pts. fumg. HNO_3 (D = 1.52) at 0° (90% yield (54)) cf.

(3) (27) (17) gives 1,3-dichloro-4-nitrobenzene [Beil. V-245, V_1-(131)], cryst. from alc., m.p. 34° (55), 33–34° (27), 33° (53) (3), accompanied by a little (2.6% at −30°, 4% at 0° (17)) 1,3-dichloro-2-nitrobenzene [Beil. V-246, V_1-(131)], m.p. 70.5° (55), 70° (56) (reactn. prod. with piperidine is 3-chloro-2-nitro-1-piperidinobenzene, m.p. 63° (57)).] — [The only other possible mononitro-*m*-dichlorobenzene, viz., 1,3-dichloro-5-nitrobenzene [Beil. V-246, V_1-(131)], m.p. 65° (55), has been prepd. indirectly.]

C̄ on dinitration, e.g., with 3.4 wt. pts. HNO_3 ($D = 1.54$) + 6.8 wt. pts. conc. H_2SO_4 at 99° for 1 hr. (56) (cf. (22) (58) (27) (59) (60) (61)) gives (85% yield (56)) 1,3-dichloro-4,6-dinitrobenzene [Beil. V-265, V_1-(138)], cryst. from alc., m.p. 103° (22) (60), 102–103° (58), 102° (27), 101° (56), accompanied by 15% yield (56) of 1,3-dichloro-2,4-dinitrobenzene [Beil. V-265], m.p. 68° (56). — For f.p./compn. data and diagram for these two cpds. (eutectic, m.p. 48.1°, contg. 38% of the former) see (56). — Note that 1,3-dichloro-4,6-dinitrobenzene with piperidine in alc. boiled for 10 min. replaces 1 chlorine yielding (62) 1-chloro-4,6-dinitro-3-piperidinobenzene, yel. cryst. from alc., m.p. 119° (62); with piperidine in pyridine (requires cooling) it replaces both chlorine atoms yielding (62) 4,6-dinitro-1,3-dipiperidinobenzene, yel. lfts. from AcOH, m.p. 130–131° (62). — [Both of the other two possible dinitro-*m*-dichlorobenzenes are known, viz., 1,3-dichloro-2,5-dinitrobenzene [Beil. V_1-(138)], m.p. 114°, and 1,3-dichloro-4,5-dinitrobenzene [Beil. V-264], m.p. 98°, but have been prepd. indirectly.]

[The direct trinitration of C̄ has not been reported; of the four possible trinitro-*m*-dichlorobenzenes only one, viz., 1,3-dichloro-2,4,6-trinitrobenzene [Beil. V-275], m.p. 128°, is known.]

[C̄ on monosulfonation with fumg. H_2SO_4 at 230° (3) or with fumg. H_2SO_4 (7% SO_3) at 100° (7) or with fumg. H_2SO_4 (12% SO_3) (54) gives (82% yield (54)) 1,3-dichlorobenzenesulfonic acid-4 [Beil. XI-55, XI_1-(15)], m.p. 86° (54) (corresp. sulfonyl chloride, m.p. 54.6° (7), corresp. sulfonamide, m.p. 182° (7) (see also below)), both C̄ and its *ortho* isomer (3:6055) sulfonate with about equal ease, both much more readily than *p*-dichlorobenzene (3:0980) (use in sepns. from latter).]

[C̄ on disulfonation with fumg. H_2SO_4 (45% SO_3) at 140–150° for 5 hrs. (63) gives 1,3-dichlorobenzenedisulfonic acid-4,6 (corresp. *bis*-(sulfonyl chloride), m.p. 122–123° (63) (64), corresp. *bis*-(sulfonamide), m.p. 276° (63); unlike the corresp. 1,3-dichloro-4,6-dinitrobenzene the halogen in this disulfonic acid is unreactive (63).]

[For study of kinetics of sulfonation of C̄ see (66).]

Ⓓ **1,3-Dichlorobenzenesulfonamide-4 (2,4-dichlorobenzenesulfonamide-1):** cryst. from dil. alc., m.p. 179–180° u.c. (65). [From C̄ on treatment as directed (65) with $ClSO_3H$ followed by conv. of the intermediate 1,3-dichlorobenzenesulfonyl chloride-4, m.p. 52–53° u.c. (65), to the sulfonamide by means of $(NH_4)_2CO_3$.] — [Note that although the m.p. of this sulfonamide is practically identical with that from *p*-dichlorobenzene (3:0980) each depresses the m.p. of a mixt. with the other; the m.p.'s of the precursor sulfonyl chlorides, viz., 52–53° for C̄, 38° for the *p*-isomer, may also serve to distinguish them (65).]

3:5960 (1) Groves, Sugden, *J. Chem. Soc.* **1937**, 1783. (2) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 431 (1932). (3) Beilstein, Kurbatow, *Ann.* **182**, 97–98 (1876). (4) Koerner, [illegible] (1937). (6) Lock, *Ber.* **66**, 1530 [illegible] 5–341 (1911). (8) Narbutt, *Ber.* [illegible] -634 (1934). (10) Timmermans,

(11) von Auwers, *Ann.* **422**, 164, 168 (1921). (12) Wibaut, van der Lande, Wallagh, *Rec. trav. chim.* **56**, 65–70 (1937). (13) Smyth, Morgan, Boyce, *J. Am. Chem. Soc.* **50**, 1542 (1928). (14) Klemenc, Löw, *Rec. trav. chim.* **49**, 637 (1930). (15) Borsche, Bahr, *Ann.* **402**, 88–90 (1914). (16) Haeussermann, *Ber.* **33**, 940–941 (1900). (17) Holleman, Reiding, *Rec. trav. chim.* **23**,

359–360, 369–379 (1904). (18) Chattaway, Evans, *J. Chem. Soc.* **69**, 850–851 (1896). (19) Raiford, Oberst, *Am. J. Pharm.* **107**, 242–244 (1935). (20) Hodgson, Walker, *J. Chem. Soc.* **1935**, 530.

(21) Sandmeyer, *Ber.* **17**, 2652 (1884). (22) Davies, Hickox, *J. Chem. Soc.* **121**, 2648–2649 (1922). (23) Kinzlberger and Co., Ger. 280,379, Nov. 26, 1914; *Cent.* **1915**, I 104. (24) Schmidt, Wagner, *Ann.* **387**, 164–165 (1911). (25) Norris, Klemka, *J. Am. Chem. Soc.* **62**, 1434 (1940). (26) Lock, Rodiger, *Ber.* **72**, 868–870 (1939). (27) Crossley, Haas, *J. Chem. Soc.* **83**, 502–503 (1903). (28) Wibaut, van der Lande, Wallagh (to Dow Chem. Co.), U.S. 2,123,857, July 12, 1938; *Cent.* **1939**, I 250; *C.A.* **32**, 7058 (1938). (29) Mouneyrat, Pouret, *Compt. rend.* **127**, 1027 (1898). (30) Olivier, *Rec. trav. chim.* **39**, 411–413 (1920).

(31) Cohen, Hartley, *J. Chem. Soc.* **87**, 1364 (1905). (32) von der Linden, *Ber.* **45**, 415–416 (1912). (33) Fisk, Noyes, *J. Am. Chem. Soc.* **58**, 1707–1714 (1936). (34) E. L. St. John, N. B. St. John, *Rec. trav. chim.* **55**, 587 (1936). (35) Wilson, Cheng, *J. Org. Chem.* **5**, 223–226 (1940). (36) Jaeger, *Z. anorg. allgem. Chem.* **101**, 143–144 (1917). (37) Böeseken, *Rec. trav. chim.* **27**, 8–9 (1908). (38) Roberts, Turner, *J. Chem. Soc.* **1927**, 1846. (39) Kunckell, *Ber.* **40**, 1702–1703 (1907). (40) I.G., Swiss 126,404, June 16, 1928; 127,692–127,703, Sept. 1, 1928; 128,366, Oct. 16, 1928; *Cent.* **1929**, I 1271–1272.

(41) Meisenheimer, Hanssen, Wächterowitz, *J. prakt. Chem.* (2) **119**, 350–355 (1928). (42) Goldberg, *J. Chem. Soc.* **1931**, 2829–2830. (43) Gubelmann, Weiland, Stallmann (to Newport [illegible] (44) [illegible] 9,844, [illegible] 1915). [illegible] m. (3) [illegible] Chem. [illegible], Brit. [illegible]

(51) Booth (to Swann Research, Inc.), U.S. 1,954,469, April 10, 1934; *Cent.* **1934**, II 1846. (52) Haeussermann, *Ber.* **34**, 38–40 (1901). (53) Roberts, Turner, *J. Chem. Soc.* **127**, 2011 (1925). (54) van de Lande, *Rec. trav. chim.* **51**, 98–99 (1932). (55) Kremer, Bendich, *J. Am. Chem. Soc.* **61**, 2659–2660 (1939). (56) Dann, *J. Chem. Soc.* **1929**, 2460–2462. (57) Loudon, *J. Chem. Soc.* **1940**, 1 [illegible] *Cent.* **1930**, I 1124; [illegible] 437 (1920). (60) H [illegible]

(61) Zincke, *Ann.* **370**, 302, Note (1909). (62) LeFevre, Turner, *J. Chem. Soc.* **1927**, 1118. (63) Davies, Poole, *J. Chem. Soc.* **1927**, 1122–1123. (64) Pollak, Wienerberger, *Monatsh.* **35**, 1472 (1914). (65) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 511–514 (1940). (66) Dresel, Hinshelwood, *J. Chem. Soc.* **1944**, 649–652.

—— **1,3-DICHLOROPROPANONE-2** (*sym.*-Dichloroacetone) CH_2—C—CH_2 (Cl, O, Cl) $C_3H_4OCl_2$ **Beil. I - 655**
I_1-(344)
I_2-(719)

B.P. 173° **M.P. 44°**

See **3:0563**. *Division A: Solids.*

3:5970 γ-CHLORO-*n*-BUTYRYL CHLORIDE $C_4H_6OCl_2$ **Beil. II - 278**

$CH_2.CH_2.CH_2.C{=}O$ (Cl, Cl) **II_1-(124)**
II_2-(254)

B.P. 173–174° (1)		D_4^{20} = **1.2581** (5)	n_D^{20} = **1.4631** (2)
83–85° at 40 mm. (2)			**1.46164** (5)
68° at 15 mm. (3)			
60–61° at 12 mm. (4)			
55–56° at 12 mm. (5)			
59–60° at 11 mm. (6)			

[For prepn. of $\bar{C}$ from γ-chloro-n-butyric acid (3:0020) with $SOCl_2$ (82% yield (4)) (3) in pet. eth. (6), or with PCl_5 (1) (3), see indic. refs.: from n-butyryl chloride (3:7370) with Cl_2 (7) or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (30% $\bar{C}$ + 15% α- and 55% β-isomers (2)) see indic. refs.]

[$\bar{C}$ with EtZnI at −15 to −20° yields (3) γ-chloro-n-propyl ethyl ketone (6-chlorohexanone-3) [Beil. I_1-(355), I_2-(747)], b.p. 182–183° at 761 mm. (8) (semicarbazone, m.p. 98–99° (8), 118° (3); p-nitrophenylhydrazone, m.p. 106–107° (3)), but above 0° the reactn. yields γ-chloro-n-propyl-ethyl-carbinyl γ-chloroacetate, b.p. 172–174° at 19 mm. (3).]

$\bar{C}$ on hydrolysis with aq. yields γ-chloro-n-butyric acid (3:0020).

For the amide, anilide, p-toluidide, and other derivs. corresp. to $\bar{C}$ see γ-chloro-n-butyric acid (3:0020).

3:5970 (1) Henry, *Bull. soc. chim.* (2) **45**, 341 (1886). (2) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (3) Wohlgemuth, *Ann. chim.* (9) **2**, 307, 405–408 (1914). (4) Blicke, Wright, Zienty, *J. Am. Chem. Soc.* **63**, 2489 (1941). (5) Leimu, *Ber.* **70**, 1050 (1937). (6) Lipp, Caspers, *Ber* **58**, 1012–1013 (1925). (7) Michael, *Ber.* **34**, 4051–4053 (1901). (8) Boosere, *Bull. soc. chim. Belg.* **32**, 29 (1923).

3:5975 ISOPROPYL TRICHLOROACETATE $C_5H_7O_2Cl_3$ Beil. S.N. 160

$(CH_3)_2CH.O.CO.CCl_3$

B.P.						
173.9–174.9°		(1)	D_4^{25} = **1.2911**	(2)	n_D^{25} = **1.4409**	(2)
173.5°	at **747** mm.	(2)	D_4^{20} = **1.3034**	(3)	n_D^{20} = **1.44355**	(3) cf. (5)
65.5–67.0°	at **15** mm.	(3)				
65°	at **10** mm.	(4)	D_4^{15} = **1.2987**	(4)	n_D^{15} = **1.4440**	(4)

[For prepn. from isopropyl alc. (1:6135) + trichloroacetic ac. (3:1150) (57.8% yield (2) (3)) see (2) (3); for prepn. from propylene + trichloroacetic ac. (3:1150) + BF_3 (48.8% yield (2)) see (2).]

[For study of chlorination of $\bar{C}$ see (4); for reaction with C_6H_6 + BF_3 yielding ethylbenzene (1:7410) see (6).]

[For study of hydrolysis of $\bar{C}$ see (3).]

3:5975 (1) Cheng, *Z. physik. Chem.* **B-24**, 310 (1934). (2) Dorris, Sowa, Nieuwland, *J. Am. Chem. Soc.* **56**, 2689–2690 (1934). (3) Palomaa, Salmi, Korte, *Ber.* **72**, 797 (1939). (4) Gayler, Waddle, *J. Am. Chem. Soc.* **63**, 3358–3359 (1942). (5) Schjanberg, *Z. physik. Chem.* **A-172**, 229 (1935). (6) McKenna, Sowa, *J. Am. Chem. Soc.* **59**, 1204–1205 (1937).

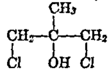
—— p-DICHLOROBENZENE

$C_6H_4Cl_2$ Beil. V - 203
V_1-(111)
V_2-(154)

B.P. 174° at 764 mm. **M.P. 53°**

See 3:0980. *Division A: Solids.*

3:5977 1,3-DICHLORO-2-METHYLPROPANOL-2 $C_4H_8OCl_2$ Beil. I-382
(sym.-Dichloro-ter-butyl alcohol) I_1— I_2—



B.P. 174–175° (1)		D_4^{20} = 1.2758 (3)	n_D^{20} = 1.4760 (3)
173–174° (2)		1.2745 (8)	1.47437 (8)
168–170.5° at 751 mm. (3)			
72–73° at 23 mm. (4)		D_4^{19} = 1.266 (6)	n_C^{19} = 1.4662 (6)
71–72° at 18 mm. (5)			
73–75° at 15 mm. (6)			
70° at 14.2 mm. (7)			
69° at 14 mm. (8)			
55–56° at 10 mm. (3)			

[*See also the isomeric 1,1-dichloro-2-methylpropanol-2* (3:5772).]

Č with aq. forms a const.-boilg. mixt., b.p. 98.3°, contg. 35.2% Č (8). — Soly. of Č in aq. at 20° is 9.4 g. Č in 100 g. aq.; soly. of aq. in Č at 20° is 10.8 g. aq. in 100 g. Č (8).

PREPARATION OF Č

[For prepn. of Č from 1-chloro-2-methylpropene-2 (methallyl chloride = isobutenyl chloride) (3:7145) by addn. of HOCl with HOCl (yields: 33% (4), 32% (3)) (7), with Cl_2/aq. (70% yield (8)), or with organic hypochlorites (7) see indic. refs.; note that if the initial methallyl chloride conts *β,β*-dimethylvinyl chloride (isocrotyl chloride) (3:7120) the crude HOCl addn. prod. will contain 1,1-dichloro-2-methylpropanol-2 (3:5772), but this can be separated from Č by fractional distillation.]

[For prepn. of Č from *α,α'*-dichloroacetone (3:0563) with MeMgBr (yields: 80–85% (6), 40% (5)) (1) see indic. refs.; from chloroacetone (3:5425) with diazomethane via *β*-methyl epichlorohydrin (3-chloro-2-methyl-1,2-epoxypropane) (3:7657) and subsequent ring opening with conc. HCl see (2).]

CHEMICAL BEHAVIOR OF Č

WITH INORGANIC REACTANTS

Dehydration. [Č is difficult to dehydrate but on twice htg. with equal wt. P_2O_5 at 110–195° for 2 hrs. gives (46% yield (6)) 1,3-dichloro-2-methylpropene-1 (3:5590). — Č with strong H_2SO_4 loses H_2O giving (9) 80% 3-chloro-2-(chloromethyl)propene-1 (3:5633) + 20% 1,3-dichloro-2-methylpropene-1 (3:5590).]

Dehydrohalogenation. Č with aq. $Ca(OH)_2$ loses 1 HCl giving (93% yield (10) (11)) 3-chloro-2-methyl-1,2-epoxypropane (*β*-methylepichlorohydrin) (3:7657) which distils as its azeotrope, b.p. 89.8°, contg. 25.6% aq. (10). — Note that, if alk. is added in excess, reactn. is complete in a few seconds at room temp. and the process can even be used as a method for detn. of Č in aq. soln. [For use of Č in comml. prepn. of *β*-methylepichlorohydrin (3:7657), *β*-methylglycerol monochlorohydrin, *β*-methylglycidol, and *β*-methylglycerol see (10).]

Behavior with sodium sulfite. [Č (1 mole) with aq. Na_2SO_3 (2 moles) at 70–90° for 2 hrs. yields (3) the salt of 2-methylpropanol-2-disulfonic acid-1,3; this prod. with PCl_5 not only is converted to the *bis* (acid chloride) but simultaneously loses H_2O yielding (3) 2-methylpropen-1,3-*bis*-(sulfonyl chloride), long ndls. from CCl_4, C_6H_6, or pet. ether, m.p.

[For prepn. of $\bar{C}$ from o-dichlorobenzene (3:6055) by partial hydrol. with aq. MeOH or EtOH alk., alk. earths, or alk. carbonates in pres. of Cu or Cu salts at elevated temps. under press. see (38)–(46) incl.]

[$\bar{C}$ in excess dil. aq. KOH with H_2 in pres. of Ni absorbs 1 mole H_2 (47) but more slowly than m-chlorophenol (3:0255) or p-chlorophenol (3:0475). — $\bar{C}$ is not reduced with HI in AcOH at 25° (48).]

[$\bar{C}$ on oxidn. with 35% peracetic acid at 25° gives slowly (17 days) in small yield (49) α-chloromuconic acid (2-chlorobutadiene-1,3-dicarboxylic acid-1,4), m.p. 190° (49), + 5-chlorohexadiene-2,4-al-6-oic acid-1, m.p. 145° (49).]

[$\bar{C}$ with Cl_2 (2 moles) in AcOH gives (80% yield (50)) 2,4-dichlorophenol (3:0560); $\bar{C}$ with Cl_2 (3 moles) undoubtedly gives 2,4,6-trichlorophenol (3:1673). — For study of chlorination of $\bar{C}$ with HOCl see (51).]

$\bar{C}$ with Br_2 (1 mole) in CCl_4 gives (87% yield (52)) 4-bromo-2-chlorophenol, ndls. from lgr., m.p. 48–49° (52), 49–50° (53), 50–51° (54). — $\bar{C}$ with Br_2 (2 moles) in aq. KBr soln. gives (55) 2-chloro-4,6-dibromophenol [Beil. VI-203], ndls. from alc., m.p. 76° cor. (55), 75–76° (56). — $\bar{C}$ with large excess Br_2 in pres. of Fe powder gives (57) 2-chloro-3,4,5,6-tetrabromophenol, ndls. from alc. or AcOH, m.p. 224° (57).

[$\bar{C}$ in aq. alk. with I_2/KI soln. as directed (55) gives 2-chloro-4,6-di-iodophenol, ndls. from alc., m.p. 96° (55). — For study of iodination of $\bar{C}$ see (58).]

[$\bar{C}$ on nitrosation as directed (59) (60) gives (96% yield (60)) 2-chloro-4-nitrosophenol (2-chlorobenzoquinone-1,4-oxime-4) [Beil. VII-631, VII_1-(346)], pale yel. ndls. from C_6H_6, m.p. 145° (60), 142° (59); for discussion of tautomerism of this cpd. see also (61) (62) (63).]

[$\bar{C}$ on mononitration, e.g., with cold mixt. of equal pts. HNO_3 (D = 1.36) + aq. (13), with HNO_3 in MeOH (64), or with HNO_3 (D = 1.5) in AcOH (65), gives a mixt. of 2-chloro-4-nitrophenol [Beil. VI-240], ndls. from aq., m.p. 110–111°, and (32% (65)) 2-chloro-6-nitrophenol [Beil. VI-239], ndls. from aq., m.p. 70–71°; of these only the latter is volatile with steam (use in detn. of $\bar{C}$ in mixts. with 4-chlorophenol (3:0475) (27)). — Both of the other mononitro-o-chlorophenols are known but have been obtd. only by indirect means; e.g., 2-chloro-3-nitrophenol, m.p. 120.5° (66), 120° (67), and 2-chloro-5-nitrophenol, m.p. 119.5° (66).]

$\bar{C}$ on dinitration, e.g., by soln. in HNO_3 (D = 1.36) and subsequent warming yields (68) 2-chloro-4,6-dinitrophenol [Beil. VI-259, VI_1-(128)], cryst. from alc., m.p. 113° (68); this prod. (unlike picric acid) is volatile with steam from H_2SO_4 soln. (use in anal. of mixts. of $\bar{C}$ with phenol (17)).

[$\bar{C}$ in alk. soln. couples with diazotized aniline giving (70% yield (69) (70) (71)) 3-chloro-4-hydroxyazobenzene (2-chlorobenzoquinone phenylhydrazone-4) [Beil. XVI-120], yel. pr. from aq. alc., m.p. 88.5° (69), 88° (70), 86° (71). — For study of corresp. coupling of $\bar{C}$ with diazotized p-nitroaniline see (72).]

[For mercuration of $\bar{C}$ and use of products as seed disinfectants, etc., see (73); for condens. prods. of $\bar{C}$ with C_6H_5.Hg.OH see (74).]

[$\bar{C}$ over pumice in a silica tube at dull red heat (75) or K salt of $\bar{C}$ + K phenolate at 250° for 8 hrs. (81) yields diphenylene dioxide [Beil. XIX-44, XIX_1-(618)], ndls. from MeOH, m.p. 119°, readily identified by dinitration with fumg. HNO_3 in AcOH (75) to dinitrodiphenylene dioxide, ndls. from pyridine, m.p. 257° (75).]

Condensation reactions involving nuclear hydrogens. [$\bar{C}$ with formalin (1:0145) in pres. of conc. HCl treated with HCl gas as directed (76) gives 3-chloro-4-hydroxybenzyl chloride, m.p. 92–93° (76). — $\bar{C}$ with formalin + H_2SO_4 (60%) at 60–65° for 16 hrs. gives (76) 3,3'-dichloro-4,4'-dihydroxydiphenylmethane, m.p. 103–104° (76). — $\bar{C}$ with formalin (1:0145) + aq. 10% NaOH as directed (77) yieds acc. to conditions 3-chloro-4-hydroxybenzyl alc., pl. from C_6H_6, m.p. 123.5–124°, and/or 3-chloro-4-hydroxy-5-(hydroxymethyl)-

benzyl alc., ndls. from $CHCl_3$, m.p. 117.5–119°. — For condens. of C̄ with formalin in prepn. of synthetic tanning agents see (78).]

[C̄ with $CHCl_3$ or $CHBr_3$ (79) in pres. of aq. NaOH undergoes Reimer-Tiemann reaction yielding both 3-chloro-2-hydroxybenzaldehyde (3:1010) and 3-chloro-4-hydroxybenzaldehyde (3:4065). — C̄ with CCl_4 in alc. alk. in s.t. at 125–136° yields (80) 3-chloro-4-hydroxybenzoic acid (3:4675). — C̄ with α,α-dichlorodiphenylmethane (3:6960) + $AlCl_3$ in cold CS_2 gives (31) 3-chloro-4-hydroxyphenyl-diphenyl-carbinol, from 60% AcOH as deep orange pl. of quinonoid desmotrope, m.p. 118°, but from alc. colorless crysts. of benzenoid desmotrope (contg. ½ mole solvent), m.p. 70–72° (31); note that in hot C_6H_6, however, this reaction takes a different course yielding (31) α,α-*bis*-(*o*-chlorophenoxy)diphenylmethane, cryst. from hot alc., m.p. 191–192° (31). — C̄ with chloral hydrate (3:1270) in pres. of alk. salts condenses (82) to 3-chloro-4-hydroxyphenyl-trichloromethyl-carbinol which on hydrolysis with NaOH yields 3-chloro-4-hydroxybenzaldehyde (3:4065).]

[C̄ with $SOCl_2$ + $AlCl_3$ in CS_2 gives (85% yield (83)) *bis*-(3-chloro-4-hydroxyphenyl) sulfoxide [Beil. VI$_1$-(422)], ndls. from dil. alc. contg. HCl, m.p. 195°. — C̄ with mixt. of conc. H_2SO_4 + fumg. H_2SO_4 (25% SO_3) at 100° for 6 hrs. disulfonates to 2-chloro-4,6-disulfophenol which undergoes bimolecular condensation to the corresp. internal ester (for details see (84)).]

[C̄ with phthalic anhydride (1:0725) with $AlCl_3$ in acetylene tetrachloride (3:5750) (85) (86) (87), or with $AlCl_3$ + NaCl at 150° (88), gives (yields: 95% (85) (86), 87% (88)) 2-(3′-chloro-4′-hydroxybenzoyl)benzoic acid, cryst. from MeOH, m.p. 224–225° (85), cryst. from AcOH, m.p. 219.5–220° (86), 219° (88); this prod. on ring closure with 15 pts. conc. H_2SO_4 at 150° for 1 hr. (88), or with 10 pts. conc. H_2SO_4 + 1 pt. $ZnCl_2$ at 130° for 5½ hrs. (85), or with 16 pts. 100% H_2SO_4 + 1 pt. H_3BO_3 at 195° for 1½ hrs. (86), gives (yields: 80% (85), 76% (88), 53.5% (86)) 3-chloro-2-hydroxyanthraquinone, yel. ndls. from AcOH, nitrobenzene + AcOH, or xylene, m.p. 267–268° (85), 266.5–267° (86), 266° (88). — Note that by slight variations other products are also formed; e.g., C̄ + phthalic anhydride + fumg. H_2SO_4 + H_3BO_3 at 170–200° for 10 hrs. gives (89) both chloro-hydroxy-anthraquinone and dihydroxyanthraquinone cf. (90) and at 255° gives (91) 1,2,4-trihydroxyanthraquinone (purpurin). — Note that C̄ (2 moles) with phthalic anhydride (1 mole) at 125° for 6 hrs. gives (75% yield (92)) dichlorophenolphthalein, m.p. 98°.]

Reactions of nuclear halogen of C̄. [C̄ on hydrolysis with aq. alk., alk. carbonates, or alkaline earths in pres. of cat. such as Cu or Cu salts at elevated temps. and under press. yields (93) (94) (95) (96) (97) (98) pyrocatechol (1:1520) cf. (43). — C̄ on fusion with KOH yields (13) pyrocatechol but some resorcinol (1:1530) is also formed (98) (99). — C̄ with aq. Na_2S + NaOH at 210–215° for 24 hrs. yields (100) 2-mercaptophenol [Beil. VI-793], b.p. 216–217° cor., m.p. +5°.]

Reactions of the phenolic group of C̄ (see also under Ⓓ, below). C̄ behaves as a weak acid; e.g., C̄ dis. in conc. aq. Na_2CO_3 soln. on shaking at room temp. (dif. and sepn. from phenol (18)) and is repptd. by treatment with CO_2 (18). — Dissoc. const. of C̄ in aq. = 32×10^{-10} (101); for studies of dissoc. const. in 50% MeOH at 20° (7) (101) (102), in 25% EtOH at 25° (103), in 30% EtOH at 25° (4) (102) see indic. refs.

C̄ has bactericidal (104) (105) (106) (107) (108) (109) and fungicidal (110) properties.

[C̄ with alkali metals gives corresp. alk. *o*-chlorophenolates; for use of these as antioxidants in motor fuels see (111). — Dry Na *o*-chlorophenolate with CO_2 at 140–150° under press. yields (25) 3-chloro-2-hydroxybenzoic acid (3-chlorosalicylic acid) (3:4745).]

[C̄ in MeOH/KOH with MeI in s.t. at 130° (112), or C̄ with aq. KOH + Me_2SO_4 at ord. temp. (113), yields *o*-chlorophenyl methyl ether (*o*-chloroanisole) (3:6255). — C̄ in abs. alc. + NaOEt with EtI yields (115) *o*-chlorophenyl ethyl ether (*o*-chlorophenetole) (3:5735). — C̄ with allyl bromide in acetone + aq. + NaOH gives (90% yield (116))

allyl o-chlorophenyl ether; b.p. 108–110° at 15 mm., D_{25}^{25} = 1.132, n_D^{25} = 1.5388; this prod. on reflux. 10 min. gives by Claisen rearr. (89% yield (146)) 2-chloro-6-allylphenol, b.p. 61–63° at 1 mm., n_D^{25} = 1.5447.]

[C̄ with $POCl_3$ refluxed for 8–11 hrs., $POCl_3$ distd. off, and crude product saponified yields (117) *bis*-(o-chlorophenyl)phosphoric acid, m.p. 105–106° cor. — For condens. of C̄ with triphenylphosphine oxide and use of prod. as seed disinfectant see (118); for use of C̄ in prepn. of triaryl phosphates (119) or of mixed triaryl thiophosphates (120) and use as plasticizers see indic. refs. — C̄ with PCl_5 gives on htg. (22) o-dichlorobenzene (3:6055).]

[C̄ with malic acid (1:0450) + conc. H_2SO_4 *fails* (121) to give the expected von Pechmann synthesis of 8-chlorocoumarin; however, C̄ with α-substituted acetoacetic esters + P_2O_5 condenses to corresp. chromones; e.g., C̄ with ethyl α-methylacetoacetate (1:1712) + P_2O_5 gives (27% yield (122)) 8-chloro-2,3-dimethylchromone [Beil. XVII₁-(177)], pale yel. ndls. from dil. alc., m.p. 108°; for further examples see (123). — C̄ (as sodium salt) + diethyl fumarate (1:3761) refluxed in xylene yields (124) diethyl α-(o-chlorophenoxy)-fumarate which on subsequent hydrolysis to the acid, ring closure with conc. H_2SO_4, and decarboxylation gives 8-chlorochromone, colorless ndls., m.p. 114–115° (124).]

C̄ with $AlCl_3$ evolves HCl and yields (125) $Cl.C_6H_4.O.AlCl_2$, insol. CS_2, but sol. in alc. and hydrolyzed by aq., m.p. 207–210° (125). — C̄ in 50% alc. with satd. soln. of PkOH in 50% alc. yields (126) a mol. cpd., C̄.PkOH, pale yel. ndls., m.p. 81–82° (126).

Ⓟ **$FeCl_3$ color reaction:** C̄ in aq. soln. with very dil. $FeCl_3$ gives violet coloration; C̄ in alc. with very dilute aq. $FeCl_3$ gives greenish-blue.

—— **o-Chlorophenyl acetate:** oil, b.p. 103° cor. at 15 mm., D_4^{20} = 1.2166 (18). [From C̄ with Ac_2O (4 pts.) + NaOAc (1 pt.) boiled for 10 min. (18).]

—— **o-Chlorophenyl benzoate** [Beil. IX-117]: oil, b.p. 314–316° (?) (127), 212–213° at 745 mm. (127), 155–157° at 3 mm. (127). [From C̄ + benzoyl chloride + aq. NaOH (127) (for study of rate see (129)).] [Note also that C̄ + BzCl + $AlCl_3$ in acetylene tetrachloride yields (128) the Fries rearr. prods. to be expected from o-chlorophenyl benzoate, viz., 3-chloro-4-hydroxybenzophenone, cryst. from alc. or C_6H_6, m.p. 180–181° (128), and 3-chloro-2-hydroxybenzophenone, pale yel. cryst. from alc., m.p. 92.5–93° (128).]

Ⓓ **o-Chlorophenyl m-nitrobenzoate:** pr. from lgr., m.p. 98° (18). [From C̄ with m-nitrobenzoyl chloride on shaking with 10% aq. NaOH at 35–50° (18).]

—— **o-Chlorophenyl p-nitrobenzoate:** ndls. from 85% alc., m.p. 114.5–114.8°. [From C̄ + p-nitrobenzoyl chloride in pyridine (unpublished work).]

—— **o-Chlorophenyl 3,5-dinitrobenzoate:** ndls. from 85% alc., m.p. 143.1–143.4°. [From C̄ + 3,5-dinitrobenzoyl chloride in pyridine (unpublished work).]

—— **o-Chlorophenyl benzenesulfonate:** unrecorded.

—— **o-Chlorophenyl p-toluenesulfonate:** m.p. 74° (4).

—— **o-Chlorophenyl benzyl ether:** oil, b.p. 138–140° at 3 mm. (130). [From C̄ (as Na salt) + benzyl chloride but in very poor yield (7.5% (130)); note that the products elsewhere (131) (132) seem to be questionable.]

—— **o-Chlorophenyl p-nitrobenzyl ether:** m.p. 100° (133). [From C̄ (as Na salt) with p-nitrobenzyl bromide refluxed in aq. alc. (133).]

Ⓓ **o-Chlorophenyl 2,4-dinitrophenyl ether:** greenish-yel. ndls. from alc., m.p. 99° (134). [From C̄ in equiv. amt. aq. NaOH refluxed with alc. 2,4-dinitrochlorobenzene (134). — Note that the m.p. of 75–76° reported earlier (135) for this compd. is identical with that given later (134) for the corresp. deriv. of m-chlorophenol (3:0255).]

Ⓓ **o-Chlorophenoxyacetic acid** (3:4375): m.p. 145–146° (136) (137), 143–145° (138); Neut. Eq. 186.5. [From C̄ in aq. NaOH (2 equivs.) with chloroacetic acid (1 equiv.) refluxed for 1 hr., then acidified (138) cf. (136) (137).]

Ⓓ *o*-Chlorophenyl *N*-(phenyl)carbamate: cryst. from C_6H_6, m.p. 120–121° (139). [From $\bar{C}$ + phenyl isocyanate in dry ether (139).]

Ⓓ *o*-Chlorophenyl *N*-(*p*-iodophenyl)carbamate: m.p. 156–157° (147). [From $\bar{C}$ + *p*-iodobenzazide in hot lgr. (147).]

Ⓓ *o*-Chlorophenyl *N*-(*p*-bromophenyl)carbamate: pr. from EtOAc, m.p. 141–143° cor. (140). [From $\bar{C}$ + *p*-bromobenzazide in lgr. (140).]

Ⓓ *o*-Chlorophenyl *N*-(*m*-nitrophenyl)carbamate: m.p. 114° u.c., 116° cor. (148). [From $\bar{C}$ + *m*-nitrobenzazide (148) or *m*-nitrophenyl isocyanate (148) in lgr. (148).]

Ⓓ *o*-Chlorophenyl *N*-(*p*-nitrophenyl)carbamate: ndls. from lgr., m.p. 143° cor. (141). [From $\bar{C}$ + *p*-nitrobenzazide in lgr. (141).] — [Note that corresp. deriv. of *m*-chlorophenol (3:0255) has m.p. 144° cor. (141).]

Ⓓ *o*-Chlorophenyl *N*-(3,5-dinitrophenyl)carbamate: pl. from C_6H_6, m.p. 182–183° (142). [From $\bar{C}$ + 3,5-dinitrobenzazide htd. in dry toluene (142).]

Ⓓ *o*-Chlorophenyl *N*-(3,5-dinitro-4-methylphenyl)carbamate: yel. pl. from lgr. or EtOAc, m.p. 175–176°, u.c., 180–181° cor. (143). [From $\bar{C}$ + *3,5-dinitro-4-methyl*-benzazide in lgr. (143).]

Ⓓ *o*-Chlorophenyl *N*-(α-naphthyl)carbamate: cryst. from lgr., m.p. 120° (144). [From $\bar{C}$ + α-naphthyl isocyanate in lgr. (144).]

Ⓓ *o*-Chlorophenyl *N*-(β-naphthyl)carbamate: pl. from lgr., m.p. 133–134° u.c., 136–137° cor. (145). [From $\bar{C}$ + β-naphthyl isocyanate (or azide) in lgr. (145).]

—— *o*-Chlorophenyl *N*,*N*-diphenylcarbamate: unreported.

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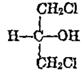
3:5985 1,3-DICHLOROPROPANOL-2 (β,β'-Dichloroisopropyl alcohol; glycerol α,α'-dichlorohydrin; "α-dichlorohydrin")



$C_3H_6OCl_2$ Beil. I - 364, I_1-(185), I_2-(383)

B.P.				
175.8–176.3° at 765 mm. (1)	D_4^{25} = **1.359** (2) (6)		n_D^{25} = **1.4797**	(2)
176° at 760 mm. (2) (6)				
175.1° at 760 mm. (3)			n_D^{20} = **1.4837**	(45)
175.5–176° at 733 mm. (4)				
174.3° at 760 mm. (5)	D_4^{17} = **1.3506**	(9)	$n_D^{16.9}$ = **1.48025**	(9)
92–92.5° at 40 mm. (2) (6)				
86° at 32 mm. (7)				
75° at 12 mm. (8)				
70–73° at 14 mm. (10)				
69° at 12 mm. (45)				

Note: Because of the great magnitude of the literature of C̄ only the most important citations can be included here; for much additional data prior to 1930, the appropriate volume of Beilstein should also be consulted.

C̄ dis at 19° in 9 pts. aq ; at 72° in 6 pts. aq., misc. with ether. [For recovery of C̄ from aq. solns. by extraction with immiscible solvents (12) (13) (14) or by steam distillation (12) (15) see indic. refs.]

[For prepn. of C̄ from glycerol (1:6540) by actn. of HCl gas at 100–110° (yield: 87% (11), 82% (6), 55–57% (10)) (12) see indic refs ; for prepn. of C̄ from 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) with fumg. HCl (yield 80% (11)) (16) (17) (1) (18), with $MgCl_2$ in dil. alc. at 125° (19), or with S_2Cl_2 (67% yield (40)) see indic. refs.; for formn. of C̄ (together with other prods.) from glycerol (1:6540) with $SOCl_2$ + pyridine see (20); from corresp. acetate (3:6318) by alcoholysis with MeOH + HCl see (21) (45); from α,α'-dichloroacetone (3:0563) reductn. with yeast see (22).]

C̄ with aq. alk. rapidly loses HCl giving 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) (yield: 90% (6), 80–90% (23), 76–81% (24-B), 67–72% (24-A), 85% (25), 79% (26)).

C̄ on oxidn. with $Na_2Cr_2O_7$ + H_2SO_4 gives (68–75% yield (27)) α,α'-dichloroacetone (3:0563). [Overoxidn. of this prod. or C̄ on oxidn. with conc. HNO_3 (28) gives chloroacetic acid (3:1370).]

[Č on reductn. with Na/Hg in moist ether gives various products including allyl alc. (1:6145), isopropyl alc. (1:6135), propylene together with epichlorohydrin (for refs. see Beil. I-364); Č htd. with HI + P in s.t. at 180° gives (29) isopropyl iodide.]

[For behavior of Č with NaSH yielding 1,3-dithioglycerol (Hg deriv. m.p. 185°, Pb deriv. m.p. 175–180° dec.) see (41).]

Č on htg. with P_2O_5 (31) or $POCl_3$ (11) (30) yields 1,3-dichloropropene-1 (3:5280).

Č on htg. with excess EtOH + NaOH yields (by a series of definite intermediate stages (25)) (6) 1,3-diethoxypropanol-2 (glycerol α,γ-diethyl ether) b.p. 108–111° at 60 mm., $D_4^{25} = 0.953$, $n_D^{25} = 1.420$ (19) (6); similarly Č on htg. with excess phenol + aq. NaOH as specified (19) gives 80% yield 1,3-diphenoxypropanol-2 (glycerol α,γ-diphenyl ether), cryst. from alc., m.p. 80–81° (19).

—— **β,β'-Dichloroisopropyl acetate:** b.p. 205° (see 3:6318).

—— **β,β'-Dichloroisopropyl benzoate:** b.p. 296° sl. dec. (12); 171–173° at 19 mm. (43), 157–160° at 12 mm. (44). [From Č + benzoyl chloride on htg. (42) or with pyridine (44).]

Ⓓ **β,β'-Dichloroisopropyl *p*-nitrobenzoate:** m.p. 59–60° (32), 58–59° (33). [From Č + *p*-nitrobenzoyl chloride with pyridine (94% yield) (33) or with quinoline in $CHCl_3$ (100% yield) (32).]

Ⓓ **β,β'-Dichloroisopropyl 3,5-dinitrobenzoate:** m.p. 129° (32). [From Č + 3,5-dinitrobenzoyl chloride + quinoline in $CHCl_3$ in 100% yield (32).]

Ⓓ **β,β'-Dichloroisopropyl benzenesulfonate:** long colorless ndls. from C_6H_6, m.p. 50° (34). [From Č + benzenesulfonyl chloride + conc. aq. NaOH (34); for study of pyrolysis see (35).]

Ⓓ **β,β'-Dichloroisopropyl *p*-toluenesulfonate:** m.p. 52–53° (36). [From Č + *p*-toluenesulfonyl chloride with conc. aq. NaOH (36).] [For use in prepn. of vat dyes of dibenzanthrone series see (37).]

Ⓓ **β,β'-Dichloroisopropyl *N*-(phenyl)carbamate:** m.p. 73–74° (20) (38), 73° (39). [From Č with phenyl isocyanate (20) (39); also indirectly from Č by conv. to corresp. chloroformate and reacting with aq. aniline (38).] [This prod. htd. a few min. with conc. aq. KOH loses HCl and ring-closes alm. quant. to 5-chloromethyl-3-phenyloxazolidone-2, pr. from hot alc., m.p. 104–105° (39).]

Ⓓ **β,β'-Dichloroisopropyl *N*-(α-naphthyl)carbamate:** m.p. 115° (38). [Prepd. indirectly from Č by conv. to corresp. chloroformate and reacting with aq. aniline (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-(α-naphthyl)-oxazolidone-2, m.p. 118° (38).]

Ⓓ **β,β'-Dichloroisopropyl *N*-(β-naphthyl)carbamate:** m.p. 101° (38). [Prepd. indirectly from Č by conv. to corresp. chloroformate and reacting with aq. aniline (38).] [This prod. with conc. aq. alk. loses HCl and ring-closes to 5-chloromethyl-3-(β-naphthyl)-oxazolidone-2, m.p. 107° (38).]

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CHAPTER XIV

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:6000–3:6499)

3:6000 *n*-PROPYL DICHLOROACETATE $C_5H_8O_2Cl_2$ Beil. II - 204
n-$C_3H_7.O.CO.CHCl_2$ II_1—
II_2-(196)

B.P. 176.7–177° at 771 mm. (1) D_4^{25} = **1.2006** (4) n_D^{25} = **1.4360** (4)
176.0–176.6° (2) D_4^{20} = **1.2240** (5) n_D^{20} = **1.4398** (5)
176° (3)

[For prepn. (70% yield (3)) from anhydrous chloral (3:5210) in *n*-propyl alc. by treatment with 1.2 moles powdered KCN see (3); for prepn. (59% yield (4)) from cyclopropane + dichloroacetic ac. (3:6208) + BF_3 see (4).]

(2) Cheng, *Z. physik. Chem.* B-24, 307 (1934).
(4) Dorris, Sowa, *J. Am. Chem. Soc.* 60, 358
2, 229 (1935)

3:6010 γ-CHLORO-*n*-PROPYL CHLOROFORMATE $C_4H_6O_2Cl_2$ Beil. S.N. 199
(γ-Chloro-*n*-propyl chlorocarbonate) $\underset{\displaystyle Cl}{\underset{|}{CH_2}}\,CH_2\,CH_2.O.CO.Cl$

B.P. 177° (1) D_{20}^{25} = **1.2946** (1) n_D^{20} = **1.4456** (1)
175–176° at 736 mm. (2)

Colorless liq.; insol. in aq. toward which it is relatively stable.

[For prepn. of $\bar{C}$ from 3-chloropropanol-1 (trimethylene chlorohydrin) (3:8285) with phosgene (3:5000) in 80% yield see (1) (2).]

$\bar{C}$ in quinoline begins to decompose into 1,3-dichloropropane (trimethylene (di)chloride) (3:5450) + CO_2 even at 35° (3) (for discussion see (4)).

$\bar{C}$ with primary arom. amines reacts as an acyl chloride yielding the corresp. γ-chloro-*n*-propyl *N*-arylcarbamates [e.g., $\bar{C}$ with *p*-aminobenzenearsonic acid (arsanilic acid) gives (92% yield (5)) γ-chloro-*n*-propyl *N*-(*p*-arsonophenyl)carbamate, m.p. 245–246° (5) cf. (6); for analogous reactions of $\bar{C}$ with *o*-aminobenzenearsonic acid (5) (6), *o*-toluidine-5-arsonic acid (5), *p*-phenetidine (1), *p*-aminobenzoic acid (1), *o*-chloroaniline (1), or *p*-chloroaniline (1) see indic. refs.]; for simpler cases see below.

Ⓓ **γ-Chloro-*n*-propyl carbamate:** cryst. from hot aq., m.p. 62° (2). [From $\bar{C}$ slowly added to 10% aq. NH_4OH (2 moles) (violent reactn. and cooling is required), yield 71% (2).]

Ⓓ γ-Chloro-*n*-propyl allophanate ($ClCH_2CH_2CH_2OCO.NH.CO.NH_2$): cryst. from hot alc., m.p. 166° (2). [From C̄ with urea (2 moles) fused for 3 hrs. (75% yield (2)).]

—— γ-Chloro-*n*-propyl *N*-phenylcarbamate: pr. from alc., m.p. 38° (2), 35–36° (1). [From C̄ with aniline (2 moles) both diluted with dry ether (3 vols.) slowly mixed in flask surrounded by ice water, ether evaporated and prod. distilled, b.p. 160–170° at 5 mm. (2); this prod. in alc. *on addn of 1 N aq. NaOH ring-closes with loss of HCl* giving (84% yield (2)) (1) 3-phenyl-tetrahydro-2-keto-1,3-oxazine, m.p. 96° (2), 94.0–94.5° (1).]

Ⓓ γ-Chloro-*n*-propyl *N*-(*o*-tolyl)carbamate: ndls. from alc., m.p. 49° (2), 46.0–46.5° (1). [From C̄ with *o*-toluidine in dry ether as for preceding case (69% yield (2)); this prod. in alc. on addn. of 1 *N* aq. NaOH ring-closes with loss of HCl giving (60% yield (2)) (1) 3-(*o*-tolyl)-tetrahydro-2-keto-1,3-oxazine, m.p. 89° (1), 87.0–87.5° (2).]

—— γ-Chloro-*n*-propyl *N*-(*p*-tolyl)carbamate: oil, b.p. 188° at 4.5 mm., $D_{20}^{20} = 1.186$, $n_D^{18} = 1.494$ (1). [*This prod. with alc. KOH (1 mole) refluxed 2 hrs. ring-closes with* loss of HCl giving (1) 3-(*p*-tolyl)-tetrahydro-2-keto-1,3-dioxazine, m.p. 127.5–128° (1).]

Ⓓ γ-Chloro-*n*-propyl *N*-(α-naphthyl)carbamate: ndls. from ether and lgr., m.p. 75.5–76.5° (1). [From C̄ with α-naphthylamine (2 moles) in aq. suspension (90% yield (1)); this prod. with alc. KOH (1 mole) refluxed 2 hrs. ring-closes with loss of HCl giving 3-(α-naphthyl)-tetrahydro-2-keto-1,3-dioxazine, m.p. 149.5–150.5° (1).]

Ⓓ γ-Chloro-*n*-propyl *N′*-anilinocarbamate (γ-chloro-*n*-propyl *N*-phenylcarbazate): cryst. from C_6H_6, m.p. 72° (7). [From C̄ with phenylhydrazine (1 mole) in aqueous pyridine (62% *yield* (7)).]

3:6010 (1) Pierce, Adams, *J. Am. Chem. Soc.* **45**, 791–794 (1923). (2) Dox, Yoder, *J. Am. Chem. Soc.* **45**, 725–726 (1923). (3) Carré, Passedouet, *Compt. rend.* **201**, 899 (1935). (4) Carré, Passedouet, *Bull. soc. chim.* (5) **3**, 1073–1082 (1936). (5) Rodewald, Adams, *J. Am. Chem. Soc.* **45**, 3102–3105 (1923). (6) Adams, Rodewald (to Abbott Laboratories), Brit. 255,971, Aug. 26. 1926; *Cent.* **1927**, I 1744, *C.A.* **21**, 2908 (1927). Can. 254,983, Oct. 27, 1925, *Cent.* **1927**, I 1744; *C.A.* **20**, 424 (1926). (7) Dox, *J. Am. Chem. Soc.* **48**, 1952 (1926).

3:6025 ***β,β′*-DICHLORODIETHYL ETHER** $C_4H_8OCl_2$ Beil. I —

(*bis*-(β-Chloroethyl) ether; "chlorex") $ClCH_2CH_2$–O–CH_2CH_2Cl I_1— I_2-(335)

B.P. 177–178° cor.	(1)	**M.P. −24.5°** (2)	D_4^{20} = **1.2095** (3)	
176° at 744 mm.	(2)			n_D^{20} = **1.457** (1)
80–82° at 20–22 mm.	(3)		D_{20}^{20} = **1.213** (1)	
70° at 15 mm.	(2)			
60° at 12 mm.	(2)			

Colorless oil with pleasant ethereal odor. — [For data on surface tension and parachor see (4); for vapor-press. data see (5).]

[For prepn. from ethylene chlorohydrin (3:5552) see (1); for use in prepn. of di-(β-chloroethyl) sulfate see (12).] [Note that C̄ forms with ethylene chlorohydrin (3:5552) a const.-boilg. mixt., b.p. 128.2°, contg. 8.2 mole % C̄ (15).]

The halogen atoms of C̄ are very unreactive to most reagents; C̄ is extremely resistant to hydrolysis, gives no Friedel-Crafts reaction with $C_6H_6 + AlCl_3$, no reaction with KCN, and is unaffected by $NaOH + As_2O_3$ (2).

C̄ on htg. with solid KOH yields (6) (7) (9) (3) divinyl ether (1:7800) (accompanied by some β-chloroethyl vinyl ether (3:7464) q.v.), but C̄ on htg. with dimethylaniline or quinoline fails to react at all, even to form quaternary salts (6).

C̄ on htg. with excess sodium alcoholates for 3–15 hrs. gives 36–45% yields of the corresponding liquid *bis* ethers (8); C̄ in alc. refluxed overnight with an excess of Na phenolates yields corresponding *bis* ethers (9); e.g., C̄ with Na α-naphtholate gives 52% yield *bis* [β(α-naphthoxy)ethyl] ether, m.p. 87° (9); C̄ with Na β-naphtholate gives 56% yield *bis*-[β-(β-naphthoxy)ethyl] ether, m.p. 122° (9).

C̄ on htg. with aniline (3 moles) for 2 hrs. at 200° gives (65% yield (9)) 4-phenylmorpholine, white flakes from 50% alc., m.p. 57–58° (1). [The crude prod. may also cont. *bis*-(β-anilinoethyl) ether, pl. from alc., m.p. 115.5° (9).] [For similar prepn. (77% yield (9)) of *N*-(p-tolyl)morpholine, m.p. 51° (8); *N*-(α-naphthyl)morpholine (68% yield (9)), m.p. 83° (8); *N*-(β-naphthyl)morpholine (72% yield (9)), m.p. 90° (8), see (8) (9).] [For corresp. reaction of C̄ with phenylhydrazine, p-phenylenediamine, and benzidine see (10); with ethylenediamine see (11).]

—— β,β'-*bis*-(α-Naphthoxy)diethyl ether: m.p. 87° (16). [From C̄ + α-naphthol (1:1500) + aq. NaOH in s.t. at 120° for 8 hrs. (16).]

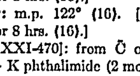
—— β,β'-*bis*-(β-Naphthoxy)diethyl ether: m.p. 122° (16). [From C̄ + β-naphthol (1:1540) + aq. NaOH in s.t. at 120° for 8 hrs. (16).]

Ⓓ *bis*-(β-Phthalimidoethyl) ether [Beil. XXI-470]: from C̄ on refluxing 3 hrs. with phthalimide + K_2CO_3 (13) or from C̄ + K phthalimide (2 moles) + trace of diethylamine on htg. 4 hrs. at 135–140° (55% yield) (9), cryst. from alc. (14), ndls. from 50% AcOH (13), m.p. 159° (9), 157° (13), 156.5° (14). [The half reaction prod., β-chloro-β'-phthalimidodiethyl ether, ndls. from lt. pet., m.p. 72° (13), 69° (9), may be sepd. from the above *bis*-ether by its much greater solubility in pet. eth. (13).]

3:6025 (1) Kamm, Waldo, *J. Am. Chem. Soc.* **43**, 2223–2227 (1921). (2) Gibson, Johnson, *J. Chem. Soc.* **1930**, 2525–2530. (3) Gulyaeva, Dauguleva, *Caoutchouc and Rubber* (*U.S.S.R*) 1937, No. 1, 49–52; *Cent.* 1937, II 558; *C.A.* 32, [illegible] (4) Gallaugher, Hibbert, *J. Am.* [illegible] *Chem. Soc.* **59**, 2523 (1937). (6) [illegible] Lott, Smith, Christiansen, *J. Am.* [illegible] *J. Am. Chem. Soc.* **47**, 163–166 [illegible] **47**, 1173–1177 (1925) (10) Axe, [illegible]
(11) Hultquist, Northey, *J. Am. Chem. Soc.* **62**, 447–448 (1940). (12) Suter, Evans, *J. Am. Chem. Soc.* **60**, 536–537 (1938). (13) Baldwin, Robinson, *J. Chem. Soc.* **1934**, 1266. (14) Gabriel, *Ber.* **38**, 3413 (1905). (15) Snyder, Gilbert, *Ind. Eng. Chem.* **34**, 1519–1521 (1942). (16) Dahlen, Black, Foohey (to du Pont Co.), U.S. 1,979,144, Oct. 30, 1934; *Cent.* **1935**, I 3051; [*C.A.* **29**, 177 (1935)].

3:6035 1,1,2,3-TETRACHLOROPROPANE

$C_3H_4Cl_4$ Beil. I - 107
I_1—
I_2—



B.P. 179–180° cor. at 756.6 mm. (1) D^{15}_{15} = 1.522 (1)
179° (3)

[For prepn. of C̄ from 1,2,3-trichloropropane (3:5840) + $SbCl_5$ at 150–190° see (2); from 1,1,2-trichloropropane (3:5630) + Cl_2 + $AlCl_3$ s[illegible] (3:5280) + Cl_2 see (4); from 3,3-dichloropropene-1 (3:[illegible] 1,2-dichloroethylene (3:5030) with CH_2Cl_2 (3:5020) + [illegible] see (5).]

3:6035 (1) Romburgh, *Bull. soc. chim.* (2) **36**, 553–557 (1881). (2) Herzfelder, *Ber.* **26**, 2435 (1893). (3) Mouneyrat, *Bull. soc. chim.* (3) **21**, 621–623 (1899). (4) Hartenstein, *J. prakt. Chem.* (2) **7**, 312–313 (1873). (5) Lehmann, Bayer (to I.G.), Ger. 715,069, Dec. 16, 1941; *Cent.* **1942**, I 2584; *C.A.* **38**, 2051 (1944).

3:6050 1,1,3,3-TETRACHLOROPROPANONE-2 $C_3H_2OCl_4$ Beil. I - 656
(*sym.*-Tetrachloroacetone) $Cl_2CH-\underset{\underset{O}{\|}}{C}-CHCl_2$ I_1-(345)
I_2—

B.P. 180–182° cor. at 718 mm. (1)
179–181° (3)

[*See also* 1,1,1,3-*tetrachloropropanone-2* (*unsym.-tetrachloroacetone*) (3:6085).]

Colorless liq. with penetrating odor; produces blisters on skin. — *Eas. sol. cold aq.*, alc., ether, C_6H_6.

$\bar{C}$ with aq. readily yields a crystn. tetrahydrate, m.p. 48–49° (1) (6), 48° (2), 47–48° (3) (4) (for crystallographic data see (2), for polymorphism see (5)); this tetrahydrate loses its aq. on distn., on stdg. over H_2SO_4, or by actn. of dry HCl gas.

[For prepn. of $\bar{C}$ from phloroglucinol (1:1620) via conversion in AcOH with Cl_2 to 1,1,3,3,6,6-*hexachloro-2,4,6-triketocyclohexane* ("*hexachlorophloroglucinol*") [Beil. VII-854, VII_1-(469)], and treatment of latter with water (yield is almost quant.) (dichloroacetic acid (3:6208) is also formed) see (6); from 2,4,6-triaminophenol [Beil. XIII-569, $XIII_1$-(211)] (2), from chloroanilic acid (3:4970) (1) (7), from 3,3,5-trichlorocyclopentanetrione-1,2,4 [Beil. VII-852] (4), or from 2,2,5-trichlorocyclopentanedione-3,4-ol-1-carboxylic acid-1 [Beil. X-985] (4) by oxidn. with $KClO_3$ + HCl (other by-products are also formed and yield is low, e.g., 7% (7)) see indic. refs.; for formn. of $\bar{C}$ from isopropyl alc. (1:6135) with Cl_2 (8), from chloroacetone (3.5425) with Cl_2 at 50–70° in light (9), or from 1,1-dibromo-3,3-dichloropropanone-2 [Beil. I-658] with alc. $HgCl_2$ in s.t. at 100° for several hours (3) see indic. refs.]

[$\bar{C}$ (as tetrahydrate) on reduction with Zn + H_2SO_4 yields (1) acetone (1:5400); $\bar{C}$ on reduction with $Al(OEt)_3$, $Mg(OEt)_2$, or EtOMgCl yields (10) 1,1,3,3-tetrachloropropanol-2 (3:9037).]

$\bar{C}$ with satd. aq. $NaHSO_3$ *readily yields a* $NaHSO_3$ cpd. (3).

$\bar{C}$ with aq. alk. does *not* (3) yield chloroform; $\bar{C}$ with alk. + aniline does *not* (3) give phenylisocyanide (carbylamine test). [Dif. from the isomeric *unsym.*-tetrachloroacetone (3:6085).]

$\bar{C}$ in abs. ether with dry NH_3 gas adds 1 NH_3 giving (92% yield (2)) 1,1,3,3-tetrachloro-2-aminopropanol-2 [Beil. I-656], ndls. from C_6H_6, m.p. 110–111° dec. with prev. sublimation; this prod. is eas. sol. in cold aq. but on warming the soln. dissociates into its components. — [The action of $\bar{C}$ with aq. NH_4OH or with aniline has not been clarified cf. (3)]

[$\bar{C}$ with excess conc. aq. HCN warmed at 50–60° soon dissolves and after 12 hrs. warming (2) ppts. $\beta,\beta,\beta',\beta'$-tetrachloro-$\alpha$-hydroxyisobutyronitrile [Beil. III-318], cryst. from C_6H_6, m.p. 112–114° (2); this prod. with $AcOH/H_2SO_4$ as directed (2) yields the corresp. $\beta,\beta,\beta',\beta'$-tetrachloro-$\alpha$-hydroxyisobutyramide, cryst. from C_6H_6, m.p. 156° (2).]

$\bar{C}$ with PCl_5 on htg. gives (2) mainly 1,1,2,2,3,3-hexachloropropane (3:6525) accompanied by some 1,1,2,3,3-pentachloropropene-1 (3:6075).

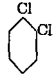
[$\bar{C}$ with diazotized aniline (4 moles) in pres. of NaOAc yields (11) dichloro-*bis*-(benzeneazo)methane, yel.-or. cryst. from hot alc., m.p. 81–82° (11); $\bar{C}$ with diazotized *p*-toluidine (4 moles) in pres. of NaOAc yields (11) dichloro-*bis*-(*p*-tolueneazo)methane, orange cryst. from C_6H_6, m.p. 159–160° (11).] [These prods. are also similarly obtd. (11) from *unsym.*-dichloroacetone (3:6085).]

D 4-(Benzeneazo)-1-phenylpyrazole [Beil. XXV-535]: golden-yel. lfts. from dil. alc. or lgr., ndls. from AcOH, m.p. 126–127° cor. (2), 126° (6). [From $\bar{C}$ in abs. alc. (2) or AcOH (6) with excess phenylhydrazine, refluxed for 5 min.]

3:6050 (1) Levy, Jedlicka, *Ann.* **249**, 89–95 (1888). (2) Levy, Curchod, *Ann* **252**, 330-349 (1889). (3) Cloëz, *Ann. chim.* (6) **9**, 182–186 (1886). (4) Hantzsch, *Ber.* **21**, 2438 (1888). (5) Schaum, Schalling, Klausing, *Ann.* **411**, 192 (1916). (6) Zincke, Kegel, *Ber.* **22**, 1467-1477; 1478–1482 (1889). (7) Levy, Witte, *Ann.* **254**, 86–88 (1889). (8) Buc (to Standard Oil Co), U S. 1,391,757, Sept. 27, 1921; *Cent.* **1922**, IV 942. (9) I.G., French 816,956, Aug. 21, 1937; *Cent.* **1938**, I 2216. (10) Meerwein, von Bock, Kirschnick, Lenz, Migge, *J. prakt. Chem.* (2) **147**, 212, 225 (1936).

(11) Favrel, *Bull. soc. chim* (5) **1**, 988–989 (1931).

3:6055 *o*-DICHLOROBENZENE



$C_6H_4Cl_2$ Beil. V - 201
V_1-(111)
V_2-(153)

B.P.	F.P.	
180.3° at 760 mm. (1)	−16.7° (1)	D_4^{25} = 1.2965 (3)
180.3° at 750 mm. (2)	−17.1° (2) (11)	1.2934 (13)
180.2° at 757.4 mm. (1)	−17.5° (10)	n_D^{25} = 1.5486 (2)
	(12) (15)	1.5476 (13)
179-181° at 755 mm. (3)		n_D^{22} = 1.5518 (1)
179.9–180.6° (4)	−17.6° (10)	D_4^{20} = 1.3048 (12)
179.5–180.5° (5)	−18° (8*a*)	1.299 (14)
179.5° at 745.2 mm. (1)		n_D^{20} = 1.5513 (2)
178.7–179.5° (6)		1.549 (14)
179° cor. (7)		n_D^{17} = 1.5532 (10)
178° at 762.5 mm. (8)		1.5524 (12)
178° at 758 mm. (8*a*)		D_4^{15} = 1.3104 (12)
86° at 18 mm. (8)		1.3085 (14)
85° at 15 mm. (9)		n_D^{15} = 1.55293 (14)
65.8° at 14 mm. (10)		D_{20}^{20} = 1.3088 (1)
		D_{15}^{15} = 1.3112 (1)

$\bar{C}$ when pure is colorless oil, volatile with steam. — Ord. comml. $\bar{C}$ conts. also the isomeric *p*-dichlorobenzene (3:0980), even as much as 25% (16); and a comml. prod. sold as insecticide conts. 40% $\bar{C}$ + 30% *p*-dichlorobenzene (3:0980) + 30% trichlorobenzene (17).

[For f.p./compn. data and diagram of system $\bar{C}$ + *p-dichlorobenzene* (3:0980) (eutectic, m.p −23.4°, contg. 86.7% $\bar{C}$) see (10) (11); for f.p./compn. data and diagram of system $\bar{C}$ + *m-dichlorobenzene* (3:5960) (eutectic, m.p. −45 9°, contg. 48.7% $\bar{C}$) see (11); for f.p./compn. data on ternary system of all three dichlorobenzenes see (10).]

[For data on densities of solns. of $\bar{C}$ in C_6H_6 (1:6400) and in *n*-hexane (1:8530) see (18); for data on D_{20}^{20} and n_D^{20} on system $\bar{C}$ + diethylbenzene (and use of the mixt. in testing fractionating columns) see (19).]

[$\bar{C}$ is very spar. sol. aq. (for study of this soly. over range 20–60° see (20).]

[For study and use of $\bar{C}$ as cleaner for metals see (21); for use as solvent for fats and oils (16) and for detn. of oils in seeds (by use of density of resultant extract (22) see indic. refs.; for use for removal of tar or pitch from surfaces coated with cellulose esters see (23); for use as solv. in purification of anthraquinone see (24); for study of toxicity of $\bar{C}$ see (25).]

[For prepn. of $\bar{C}$ from *o*-chloroaniline [Beil. XII-597, XII_1-(297)] via diazotization and use of Cu_2Cl_2 reactn. (yields: 70% (26), 25% (27)) (1) (8) (28) see indic. refs.; from *o*-phenylenediamine [Beil. XIII-6, $XIII_1$-(5)] via tetrazotization in AcOH with nitrosylsulfuric acid followed by use of Cu_2Cl_2 reactn. (70.1% yield) see (29); from 1,2-dichlorobenzenesulfonic acid-4 (see below) by distn. from strong H_2SO_4 with superheated steam at 200–240° see (30).]

[For formn. of $\bar{C}$ from 2-chlorophenol (3.5980) by htg. with PCl_5 (20% yield) see (7); from o-bromonitrobenzene [Beil. V-247, V_1-(131)] with PCl_5 in s.t. at 180° (31) or with NH_4Cl in s.t. at 320° (32) see indic. refs , from o-dinitrobenzene [Beil. V-257, V_1-(135)] with conc HCl in s t. at 250–270° see (33)]

[For formn. of $\bar{C}$ (together with m- and p-isomers in some cases) from C_6H_6 with Cl_2 in pres. of I_2 (7), $AlCl_3$ (34) (35), or $SnCl_4$ (36) see indic refs., from chlorobenzene (3:7903) with Cl_2 + cat. at 600° (11) cf. (37) or with Cl_2 in pres. of Al/Hg (38), $AlCl_3$ (gives 30% $\bar{C}$ (11)) (34), $FeCl_3$ (gives 39% $\bar{C}$ (11)), or with $Al_2S_2Cl_8$ (i.e., $2AlCl_3 + S_2Cl_2$) + SO_2Cl_2 (8a) see indic. refs.]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg (38) or $FeCl_3$ (39) (40) (41) gives mainly 1,2,4-trichlorobenzene (3:6420), but 1,2,3-trichlorobenzene (3·0990) is also formed (41). — $\bar{C}$ with Cl_2 in s t. at room temp. in sunlight as directed (42) adds $3Cl_2$ yielding o-dichlorobenzene-hexachloride, m.p. 149° (42).] — [For study of photochem chlorination of $\bar{C}$ see (43).]

[$\bar{C}$ with Mg in dry ether does not react (44)] — [$\bar{C}$ with CO + cat. at elev. temps. gives (45) benzoic acid, presumably through intermediate formn. of o-phthalic acid and subsequent loss of CO_2.]

[$\bar{C}$ with isopropyl alc (1 6135) + BF_3 + P_2O_5 under reflux gives (53% yield (87)) 3,4-dichlorocumene (3,4-dichloro-isopropylbenzene) (87)]

[$\bar{C}$ with CH_3Cl (3.7005) + $AlCl_3$ yields (30) hexamethylbenzene (1:7265) + eso-trichloromesitylene (3 8725). — $\bar{C}$ (3+ moles) with $CHCl_3$ (1 mole) + $AlCl_3$ without solv. at 55° for 8 hrs. gives (15% yield on the $CHCl_3$ (46)) tris-(3,4-dichlorophenyl)methane, white pl., m p. 160.5–162° (46) — $\bar{C}$ with CCl_4 + $AlCl_3$ presumably yields 3,4,3′,4′-tetrachlorobenzophenone dichloride (not isolated) since the reaction prod. with 95% alc. (46) or $AcOH/H_2SO_4$ (47) gives 3,4,3′,4′-tetrachlorobenzophenone, cryst. from hot alc. or hot acetone, m p. 141–142° (46), 142° (47) (accompanied in latter case (H_2SO_4) by some 3,4-dichlorobenzoic acid (3.4925), m.p 203° (47).]

[$\bar{C}$ with acetyl Cl (3:7065) + $AlCl_3$ gives (yields: 70% (49), 40% (48)) 3,4-dichloroacetophenone, b.p. 135° at 12 mm. (48), m p. 76° (48), 74° (49) (corresp. oxime, m.p. 107° (50)). — $\bar{C}$ with chloroacetyl chloride (3.5235) + $AlCl_3$ gives (50) (85) 3,4-dichlorophenacyl chloride (3,4,ω-trichloroacetophenone), m.p 43° (50), 44° (85). — $\bar{C}$ with β-chloro-n-butyric acid (3:0035) + $AlCl_3$ or conc H_2SO_4 yields (51) by condens. and subsequent ring closure a mixt. of x,y-dichloro-3-methylindanone-1 cpds.]

[$\bar{C}$ with phthalic anhydride (1·0725) + $AlCl_3$ gives (yields 80% (5), 73% (52) (53), 35% (54)) (55) o-(3,4-dichlorobenzoyl)benzoic acid, m.p 194.5° cor. (54), 192.5° (5), 191.2° cor. (52), 190° (55), this prod. on ring closure with conc. H_2SO_4 gives a mixt. of two dichloroanthraquinones consisting of 87% (54) (5) 2,3-dichloroanthraquinone [Beil. VII_1-(413)], m.p. 271° cor. (54), 268° (5), and 13% (54) (5) 1,2-dichloroanthraquinone [Beil. VII_1-(411)], m p. 196.5° cor. (54), 194 5° (5). Note that $\bar{C}$ reacts with phthalic anhydride much more readily than p-dichlorobenzene (3·0980), after making reactn. mixt. alk. any p-dichlorobenzene (as from use of crude $\bar{C}$) may be distilled out with steam (use in sepn. of p-dichlorobenzene from $\bar{C}$ (86)); note also the claim (86) that under certain conditions $\bar{C}$ with phthalic anhydride + $AlCl_3$ is claimed to replace 1 chlorine atom by hydrogen so that an o-(x-chlorobenzoyl)benzoic acid results which on ring closure with 100% H_2SO_4 gives 80% yield 2-chloroanthraquinone (3·4922). — $\bar{C}$ with 4,5-dichlorophthalic anhydride (3:4830) + $AlCl_3$ gives (80% yield (56)) 2-(3,4-dichlorobenzoyl)4,5-dichlorobenzoic acid, cryst from C_6H_6, m.p. 183° (56); this prod. with conc H_2SO_4 ring-closes giving mainly 2,3,6,7-tetrachloroanthraquinone, m.p. 348° (56), accompanied by a little 1,2,6,7-tetrachloroanthraquinone, m.p. 242° (56).]

[$\bar{C}$ on partial hydrol. with aq. MeOH alk., alk. carbonates, or best alk. earths in pres. of Cu or Cu salts at elevated temps. under press. gives in excellent yields (57) (58) (59) (60)

(61) (62) (63) (64) (65) *o*-chlorophenol (3:5980) (some phenol (1:1420) is also formed (62)); if the hydrolysis of C̄ is carried further, especially by use of aq. alk. in pres. of Ba or Sr salts and a reducing agt. (66), pyrocatechol (1:1520) is obtd. cf. (59) (61) (64).] — [For study of kinetics of reactn. of C̄ with NaOMe/MeOH at 175° see (67) (68) (69).]

[C̄ with anhyd. NH_3 in alc. in pres. of $CuCl_2$ + Cu at 200° under press. yields (70) *o*-chloroaniline; C̄ with conc. aq. NH_4OH in pres. of CuO under press. at 150–200° (71) (72) or with Na in liq. NH_3 (73) gives o-phenylenediamine.] — [C̄ with K diphenylamine gives by rearr. on htg. (74) (75) *N,N,N',N'*-tetraphenyl-*m*-phenylenediamine [Beil. XIII-42], m.p. 137.5–138° (74) (75).]

[C̄ on mononitration, e.g., at 0° with a mixt. of HNO_3 ($D = 1.52$) + conc. H_2SO_4 (75) cf. (15) (4), gives (yields: 95% (15), 67% (75)) (7) (8) (76) mainly 1,2-dichloro-4-nitrobenzene [Beil. V-246, V_1-(131)], cryst. from alc., m.p. 43° (7) (8), 42.5° (4) (reactn. prod. with piperidine is 2-chloro-4-nitropiperidinobenzene, m.p. 47–48° (78)), accompanied by a little (5.2% at −30°, 7.2% at 0° (8)) 1,2-dichloro-4,5-dinitrobenzene (see below).] — [The only other possible mononitro-isomer, viz., 1,2-dichloro-3-nitrobenzene [Beil. V-245, V_1-(130)], m.p. 61°, has been *obtd.* only by indirect means (77) (76) although prob. present (4) in the oil from the main mononitration product.]

[C̄ on dinitration, e.g., with 4 wt. pts. HNO_3 ($D = 1.52$) + 6 wt. pts. conc. H_2SO_4 at 100° for 1 hr. (79) (28) cf. (80) (or the above 1,2-dichloro-4-nitrobenzene with HNO_3 ($D = 1.5$) + fumg. H_2SO_4 (20% SO_3) 2 hrs. at 100° (78)), gives 1,2-dichloro-4,5-dinitrobenzene [Beil. V-265], cryst. from dil. AcOH, m.p. 109–110° (78), 110° (28) (79) (reactn. prod. with piperidine is 1,2-dichloro-4-nitro-5-piperidinobenzene, m.p. 62–64° (78)), accompanied (28) by a little 1,2-dichloro-3,5-dinitrobenzene [Beil. V_1-(138)], m.p. 56° (28).] — [All the other possible isomeric *o*-dichlorodinitro cpds. are known but have been obtd. only by indirect means: 1,2-dichloro-3,4-dinitrobenzene [Beil. V-264], m.p. 53–55°, 1,2-dichloro-3,6-dinitrobenzene, m.p. 60°, and 1,2-dichloro-4,6-dinitrobenzene, m.p. 56°.]

[None of the four possible 1,2-dichloro-trinitrobenzenes appears to have been reported.]

[C̄ on monosulfonation, e.g., with fumg. H_2SO_4 in s.t. at 210° for 8 hrs. (7), or at room temp. (30), or at 100° (10), or with $H_2SO_4.H_2O$ + fumg. H_2SO_4 (60% SO_3) in pres. of Hg at 100° for 1 hr. (81), gives mainly 1,2-dichlorobenzenesulfonic acid-4 [Beil. XI-55, XI_1-(16)] (Na salt less sol. aq. (81)) accompanied by a lesser amt. of 1,2-dichlorobenzenesulfonic acid-3 (Na salt more sol. aq. (81)) (some *bis*-(dichlorophenyl) sulfone, m.p. 173° (30), may also be formed during sulfonation).] — [C̄ sulfonates much more readily than *p*-dichlorobenzene (3:0980); for use in sepn. see (7) (30); for removal of chlorobenzene from mixt. with dichlorobenzenes via sulfonation of former with 95% H_2SO_4 see (11).]

Ⓓ **1,2-Dichlorobenzenesulfonamide-4 (3,4-dichlorobenzenesulfonamide-1):** cryst. from dil. alc., m.p. 134–135° u.c. (83). [From C̄ by treatment as directed (83) with $ClSO_3H$ followed by conv. of the intermediate 1,2-dichlorobenzenesulfonyl chloride-4, m.p. 18–19° (83), with $(NH_4)_2CO_3$ to the desired sulfonamide.] — [For formn. of 3,4-dichlorobenzenesulfonyl chloride with $ClSO_3H$ and use in sepn. of C̄ from *p*-dichlorobenzene see (82); for prepn. of the sulfonamide and use as plasticizer see (84).]

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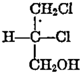
3:6060 ***d,l*-2,3-DICHLOROPROPANOL-1** (Glycerol α,β-dichlorohydrin; "β-dichlorohydrin"; allyl alcohol dichloride)



$C_3H_6OCl_2$ **Beil. I - 356** **I_1-(181)** **I_2-(370)**

B.P. 182° at 760 mm. (1)		D_4^{20} = **1.3534** (5)	
182° (2) (3) (8)			
179–181° sl. dec. (4)		D_0^{18} = **1.345** (4)	n_D^{18} = **1.4875** (4)
79–80.5° at **18** mm. (4)			
81–81.5° at **13.5** mm. (5)			
75–77° at **15** mm. (6)			

Colorless visc. liq.; spar. sol. cold aq., pet. ether; misc. with alc., ether, acetone, C_6H_6.

[For prepn. of $\bar{C}$ from glycerol (1:6540) (together with other prods.) see (1); for prepn. from allyl alcohol (1:6145) with Cl_2 + aq. (2) (7) (8) (5) (20% yield) or with Cl_2 in CS_2 (40% yield (9)) see indic. refs.; from allyl chloride (3:7035) by addition of HOCl see (10) (11) (12); from the corresp. acetate (β,γ-dichloro-*n*-propyl acetate) (3:6220) by alcoholysis using MeOH + HCl (33% yield (4)) (6); from vinyl chloride (3:7004) by reactn. with formaldehyde (30% soln.) + HCl + $CaCl_2$ see (13).]

$\bar{C}$ with aq. alk. loses HCl yielding (14) 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358). [For studies of kinetics of this loss of HCl with aq. alk. see (15); for use of $Ba(OH)_2$ hydrol. as means of detn. of $\bar{C}$ in pres. of 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985) see (16).]

$\bar{C}$ with sodium phenolate does *not* give the expected 2,3-diphenoxypropanol-1 but instead (4) (presumably by intermediate formation of epichlorohydrin (3:5358)) the isomeric 1,3-diphenoxypropanol-2, [Beil. VI-149, VI_1-(86)], m.p. 79° (4).

$\bar{C}$ on oxidn. with conc. HNO_3 (D = 1.47) yields (12) (17) (6) (18) α,β-dichloropropionic acid (3:0855), m.p. 50°. [$\bar{C}$ on reductn. with P + HI at 180° yields (8) isopropyl iodide + isopropyl chloride.]

[$\bar{C}$ with $SOCl_2$ at 100° gives (85% yield (19)) *bis*-(β,γ-dichloro-*n*-propyl) sulfite, b.p. 175° at 4 mm., $D_0^{23.7}$ = 1.501, n_D^{23} = 1.509 (19); $\bar{C}$ with SO_2Cl_2 gives (75% yield (19)) 2,3-dichloropropane-sulfonyl chloride-1, b.p. 122–123° at 15 mm., $D_0^{20.5}$ = 1.582, n_D^{23} = 1.457 (19).]

[$\bar{C}$ with PCl_5 yields (7) 1,2,3-trichloropropane (3:5840); $\bar{C}$ with NaCN gives (20) (presumably by formation and subsequent reaction of epichlorohydrin) 25% yield γ-chloro-β-hydroxy-*n*-butyronitrile; for reactn. of $\bar{C}$ with NH_3 see (21); for reactn. of $\bar{C}$ with Na_2S, NaSH, etc., yielding thioglycerols see (22).]

—— **β,γ-Dichloro-*n*-propyl acetate:** b.p. 192° (see 3:6220). [For general study of kinetics of esterification of $\bar{C}$ see (3).]

—— **β,γ-Dichloro-*n*-propyl benzoate:** oil, b.p. 180–183° at 24 mm. (4).

Ⓓ **β,γ-Dichloro-*n*-propyl *p*-nitrobenzoate:** m.p 37–38° (4), 35.5–37° (23). [From $\bar{C}$ + *p*-nitrobenzoyl chloride + pyridine (23).]

—— **β,γ-Dichloro-*n*-propyl 3,5-dinitrobenzoate:** unreported.

—— **β,γ-Dichloro-*n*-propyl benzenesulfonate:** unreported.

—— **β,γ-Dichloro-*n*-propyl *p*-toluenesulfonate:** unreported.

Ⓓ **β,γ-Dichloro-*n*-propyl *N*-phenylcarbamate:** cryst. from lgr., m p. 72–73° (24), 73–74° (25). [From $\bar{C}$ + phenyl isocyanate at 90° (24) or indirectly from β,γ-dichloro-*n*-propyl chloroformate with aniline (25).]

Ⓓ **β,γ-Dichloro-*n*-propyl *N*-(α-naphthyl)carbamate:** ndls. from alc., m.p. 93° (25).

[Prepd. indirectly from β,γ-dichloro-*n*-propyl chloroformate with α-naphthylamine (25).]

Ⓓ β,γ-Dichloro-*n*-propyl *N*-(β-naphthyl)carbamate: lfts. from alc., m.p. 99° (25). [Prepd. indirectly from β,γ-dichloro-*n*-propyl chloroformate with β-naphthylamine (25).]

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3:6075 1,1,2,3,3-PENTACHLOROPROPENE-1 C_3HCl_5 Beil. I - 200

$$Cl_2C{=}C(Cl)\,CHCl_2$$

I₁-(83)
I₂—

B.P. 183° (1) $D_4^{24} = 1.6317$ (1) $n_D^{20} = 1.5313$ (1)
116° at 9 mm. (1)

C̄ + Br_2 in sunlight gives (1) 1,2-dibromo-1,1,2,3,3-pentachloropropane, m.p. 71° (1).

C̄ with powdered KOH in toluene at 100° yields (1) a prod. C_6Cl_8, colorless ndls., m.p. 93–94° (1).

C̄ shaken with conc. H_2SO_4, poured onto ice, yields 2,3,3-trichloropropen-2-al-1 (α,β,β-trichloroacrolein) [Beil. I_1-(378)], b.p. 164° (1), m.p. 10° (1). [Oxime, m p. 101°, converted on fusion into stereoisomer, m.p. 132° (1); phenylhydrazone, yel.-br. ndls., m.p. 97–98° dec. (1).]

C̄ with conc H_2SO_4 for a longer time at 40–50°, poured onto ice, ppts. (1) α,β-dichloroacrylic ac. (3:2265), m.p. 86° (1)

3:6075 (1) Prins, *J. prakt Chem.* (2) **89**, 419–420 (1914).

3:6085 1,1,1,3-TETRACHLOROPROPANONE-2 $C_3H_2OCl_4$ Beil. I - 656
(*unsym.*-Tetrachloroacetone)

$$CH_2(Cl){-}C({=}O){-}CCl_3$$

I₁—
I₂—

B.P. 183° (1) $D_4^{15} = 1.624$ (1) $n_D^{18} = 1.497$ (1)
180–182° (2)
71–72° at 13 mm. (3)

[*See also* 1,1,3,3-*tetrachloropropanone*-2 (3:6050).]

Colorless limpid liq.; odor faint by itself but on warming or on dilution with ether shows

lachrymatory props. — Č with aq. readily yields (1) (2) (3) (4) a crystn. tetrahydrate, m.p. 46° (1), 39° (2), 65° (3).

[For prepn. of Č from isopropyl alc. (propanol-2) (1:6135) with Cl_2 in cold see (1); from acetone (1:5400) with Cl_2 see (2) (4) (5); from chloroacetone (3:5425) with Cl_2 at 50–70° in light see (6); from 1,1,1-trichloropropanone-2 (3:5620) with $SOCl_2$ at 180° see (3).]

Č reduces $NH_4OH/AgNO_3$, Fehling's soln., or aq. $KMnO_4$ instantly in cold (1) but does not give fuchsin-aldehyde test (1).

Č with NH_4OH (1) yields chloroform (3:5050) and chloroacetamide [Beil. II-199, II_1-(90), II_2-(193)], m.p. 116–117°.

Č with aq. KOH yields (1) chloroform (3:5050) together with the salts of both chloroacetic acid (3:1370) and trichloroacetic acid (3:1150). [Dif. from the isomeric *sym.*-tetrachloroacetone (3:6050).]

Č with aq. KOH + aniline yields (5) phenyl isocyanide (carbylamine reaction). [Dif. from the isomeric *sym.*-tetrachloroacetone (3:6050).]

3:6085 (1) Brochet, *Bull. soc. chim.* (3) **13**, 117–120 (1895); *Ann. chim.* (7) **10**, 134–141 (1897); *Compt. rend.* **119**, 1271 (1894). (2) Cloëz, *Ann. chim.* (6) **9**, 180–182 (1886). (3) Arndt, Amende, Ender, *Monatsh.* **59**, 215 (1932). (4) Bouis, *Ann.* **64**, 316–319 (1848). (5) Bischoff, *Ber.* **8**, 1340–1341 (1875). (6) I.G., French 816,956, Aug. 21, 1937; *Cent.* **1938**, I 2210.

3:6090 ETHYL *d,l*-α,β-DICHLOROPROPIONATE $C_5H_8O_2Cl_2$ Beil. II - 252, II_1—, II_2—

$$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH}-COOC_2H_5$$

B.P. 183–184° (1)	D_4^{20} = **1.2461** (3)	n_D^{20} = **1.44815** (3)
182–185° (3)		
76–77° at 15 mm. (2)		

[For prepn. of Č from α,β-dichloropropionic acid (3:0855) with abs. EtOH + dry HCl at 0° (74–78% yield (2)) (1) see indic. refs.; from α,β-dichloropropionyl chloride (3:9034) with EtOH see (4) (3) (5).]

Č is difficult to keep and readily loses HCl (3). — Č on htg. with dimethylaniline, quinoline, or quinaldine at 100° for 10 min. under N_2 loses HCl yielding (4) ethyl α-chloroacrylate (3:9242).

Č with $Ba(OH)_2$ both saponifies and loses HCl yielding (5) (6) α-chloroacrylic acid (3:1445), m.p. 65°.

Č reacts easily with alc. KCN, and after boilg. the resulting soln. with KOH yields (7) fumaric acid (1:0895) and *d,l*-malic acid.

Č on boilg. with 20% HCl hydrolyzes (4) yielding EtOH (1:6130) and α,β-dichloropropionic acid (3:0855) q.v.

3:6090 (1) Werigo, Melikov, *Ber.* **10**, 1500 (1877). (2) Yarnall, Wallis, *J. Org. Chem.* **4**, 287 (1939). (3) Brühl, *Ann.* **203**, 25 (1880). (4) Marvel, Dec, Cooke, Cowan, *J. Am. Chem. Soc.* **62**, 3495–3498 (1940). (5) Werigo, Werner, *Ann.* **170**, 167 (1873). (6) Otto, Beckurts, *Ber.* **18**, 243 (1885). (7) Werigo, Tanatar, *Ann.* **174**, 367–372 (1874).

e (1) (10) (5) (6) (11); from α,β,β-trichlorodiethyl ether + Zn (78% yield (4)), . (3), or NaOEt (12), or even water (3); from α,β,β,β-tetrachlorodiethyl ether abs. alc (13).]

rming with conc. H_2SO_4 (14) (2) or on htg. at 150° with conc. HCl (15) or on htg. ›ic anhydride + a little conc. H_2SO_4 gives (yield 81% (1), 78% (10), 71% (16)) etaldehyde (3:5180), b.p. 90–91°.

g. with alc. NaOH at 160–180° yields (17) glyoxal tetraethylacetal [Beil. I-760], (17). — $\bar{C}$ with K *ter*-butylate loses HCl yielding (5) chloroketene diethylacetal, ıt 732–740 mm., $D_{15}^{15} = 1.0534$, $n_D^{25} = 1.4375$ (5).

PCl_5 yields (15) α,β,β-trichlorodiethyl ether [Beil. I-615].

) van de Walle, *Bull. soc. chim. Belg* 28, 308–309 (1914/18). (2) Pinner, *Ann.* **179**, 75). (3) Oddo, Mameli, *Gazz chim ital.* **33**, II 412–414 (1903). (4) Neher, Fleece, *em. Soc.* **48**, 2422–2423 (1926). (5) Magnani, McElvain, *J. Am. Chem. Soc.* **60**, 2210–3) (6) Lieben, *Ann.* **104**, 114–115 (1857) (7) I G, French 814,435, June 23, 1937; , II 3066, *C A* **32**, 1390 (1938). (8) Ger. 528,194, June 26, 1931; *Cent.* **1931**, II 1910. ı, *Ann.* **279**, 300 (1894). (10) Böeseken, Tellegen, Plusje, *Rec. trav. chim.* **57**, 75 (1938). attaway, Backeberg, *J. Chem. Soc.* **125**, 1101 (1924). (12) Jacobsen, *Ber.* **4**, 217 (1871). r, Foster, *J. Am. Chem. Soc.* **31**, 414 (1909). (14) Paterno, *Ann.* **149**, 373 (1869). , *Jahresber.* **1876**, 475 (16) Wohl, Roth, *Ber.* **40**, 217 (1907). (17) Pinner, *Ber.* **5**, 1872).

d,l-α-CHLOROPROPIONIC ACID $C_3H_5O_2Cl$ Beil. II - 248

(2-Chloropropanoic acid) CH_3—CH.COOH II_1-(110)

| (with Cl on the CH) II_2-(226)

Cl

B.p.		Ref.		
186° cor.		(1)	D_4^{20} = **1.2585** (6)	n_D^{20} = **1.4350** (6)
186°		(2)		
185.2°	at 760 mm.	(3)		$n_D^{19.4}$ = **1.4364** (3)
185°		(4)		
88.6–89.4°	at 15 mm.	(3)		
83.5–84.5°	at 12 mm.	(5)		

less liq with weak odor suggestive both of acetic acid and butyric acid; misc. with or ether; volatile with steam, blisters skin.

prepn. of $\bar{C}$ from propionic acid (1:1025) with Cl_2 (7) (8) or with SO_2Cl_2 + dibenzoyl e in CCl_4 (9) see indic. refs.; from α-chloropropionyl chloride (3:5320) by hydrolysis) (11) (12) with water see indic. refs.; from α-chloropropionitrile by hydrolysis with ICl see (5); from 2-chloropropanol-1 (3:7917) (4) or from 3-chlorobutanone-2 (α-thyl methyl ketone) (3:7598) (13) (14) by oxidn. with HNO_3 or other oxidn. agts. ic. refs.]

n treatment with Cl_2 as specified (15) yields α,β-dichloropropionic acid (3:0855); ı $SOCl_2$ yields (16) α-chloropropionyl chloride (3:5320), b.p. 111°; $\bar{C}$ on reduction n + HCl yields (10) propionic acid (1:1025) [for study of catalytic hydrogenation or its salts see (17)]; $\bar{C}$ with SO_3 at 170° yields (18) α-chloro-α-sulfopropionic acid actn. of $\bar{C}$ with sulfites see (2)], $\bar{C}$ with conc. aq. NH_4OH gives (43–46% yield (19)) nine (α-aminopropionic acid) [for behavior of $\bar{C}$ with liq. NH_3 see (20) (21)].]

n alk. hydrolysis gives (10) (22) lactic acid (1:0400) [for study of rate of hydrolysis 23) or its sodium salt (24) see indic. refs.].

on htg. with pyridine at 100° loses CO_2 and yields (25) ethylpyridinium chloride.]

n conversion to salt, treatment with KCN, and subsequent acidification yields (26) ylmalonic acid, m.p. 132° (has been used for ident. of $\bar{C}$ (26)).

[C̄ with Cl_2 in pres. of Fe gives (16) dichloromaleyl (di)chloride (3:6197) q.v. — C̄ with Br_2 in dark does not react, but in direct sunlight for 5 hrs. adds 82% of theoretical amt. yielding (2) α-chloro-α,β-dibromosuccinyl (di)chloride, b.p. 116–118° at 10 mm. (2), which on hydrolysis with aq. gives (2) α-chloro-α,β-dibromosuccinic acid, hydrated pr. from HCl, m.p. 65–75°, which after drying over conc. H_2SO_4 gives anhydrous form, m.p. 139–140° (2).]

[C̄ with 3 *N* EtOH/KOH (large excess) in freezing mixt. loses HCl and hydrolyzes (or vice versa) and after acidification as directed gives K H acetylenedicarboxylate which with aq. at 100° for 1 hr. loses CO_2 giving (39% yield from C̄ (12)) propiolic acid [Beil. II-477, II_1-(208), II_2-(449).]

[C̄ with MeOH under reflux yields (13) dimethyl chlorofumarate (3:6582); C̄ with EtOH yields (1) (9) (15) diethyl chlorofumarate (3:6864); note that C̄ reacts with MeOH or with aniline much more rapidly than the isomeric chloromaleyl (di)chloride (3:6158) (for details and graphs see (2)).]

C̄ (1 mole) with chlorofumaric acid (3:4853) (1 mole) at 125° for 1 hr. gives (11) chloromaleic anhydride (3:0280), m.p. 33°.

[C̄ with $AlCl_3$ combines yielding a viscous oil, solidifying in freezing mixt. to yel. cryst., m.p. about 50°; this prod. with water regenerates C̄ but if first htd. at 100° for several hrs. and then treated with aq. gives (85–87% yield (2)) (3) chloromaleyl (di)chloride (3:6158).]

C̄ with excess conc. aq. NH_4OH *reacts vigorously yielding* (1) (11) *chlorofumaric* acid diamide, ndls. from alc., m.p. 187° (11).

[C̄ in aq. AcOH (1:4) with hydrazine hydrate as directed gives hydrazine salt of *N,N*-*bis* (α-chloro-β-carboxyacryloyl)hydrazine (?), m.p. 218° (9); note that C̄ with $NH_2.NH_2.H_2O$ in ether, pet. eth., or AcOH gives only (9) resinous or amorphous yel. prods.]

C̄ (1 mole) with *p*-chloroaniline (4 moles) in dry ether reacts vigorously giving mainly (11) chlorofumaro-di-*p*-chloroanilide, pale yel. ndls. from alc., m.p. 223° (11), accompanied by a little *N*-(*p*-chlorophenyl)chloromaleimide, pl. from alc. mother liquor, m.p. 175° (11).

C̄ on hydrolysis with aq. yields chlorofumaric acid (3:4853), m.p. 193°.

3:6105 (1) Perkin, *J. Chem. Soc.* **53**, 695–697, 700 (1888). (2) Ott, *Ann.* **392**, 258–259, 263–264, 278–285 (1912). (3) Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* **1933**, 15–21. (4) von Auwers, Schmidt, *Ber.* **46**, 481 (1913). (5) Ruggli, *Helv. Chim. Acta* **3**, 569 (1920). (6) Diels, Thiele, *Ber.* **71**, 1174–1175 (1938). (7) Gladstone, *J. Chem. Soc.* **59**, 293 (1891). (8) von Auwers, Harres, *Ber.* **62**, 1679 (1929). (9) Ruggli, Hartmann, *Helv. Chim. Acta* **3**, 512–514 (1920). (10) Perkin, Duppa, *Ann.* **115**, 105–107 (1860).

(11) Chattaway, Parkes, *J. Chem. Soc.* **125**, 466–468 (1924). (12) Ingold, *J. Chem. Soc.* **127**, 1202–1203 (1925). (13) Kauder, *J. prakt. Chem.* (2) **31**, 24–38 (1885). (14) Zetsche, Hubacher, *Helv. Chim. Acta* **9**, 292–293 (1926). (15) Claus, *Ann.* **191**, 80–93 (1878). (16) Vandevelde, *Bull. acad. roy. Belg.* (3) **37**, 680–700 (1899); *Cent.* **1900**, I 404.

3:6110 DICHLOROACETALDEHYDE DIETHYLACETAL ("Dichloroacetal")

$C_6H_{12}O_2Cl_2$ — $Cl_2.CH.CH(OC_2H_5)_2$ — Beil. I - 614, I_1-(328), I_2-(677)

B.P. 185–186°	(1)	$D^{14}_{14} = 1.1383$ (6)
183–184°	(2)	
182–184°	(3)	
181–184°	(4)	
178–181° at 760 mm.	(5)	
66–71° at 12 mm.	(5)	

C̄ undergoes sl. decompn. on stdg. or distn. — [For use as insecticide see (7) (8).]

[For prepn. of C̄ from acetaldehyde diethylacetal (1:0156) by actn. of Cl_2 (37% yield (5)) see (5) (17); from ethyl alcohol (1:6130) by actn. of Cl_2 (yield 75% (1), 40% (10),

0% (5)) see (1) (10) (5) (6) (11); from α,β,β-trichlorodiethyl ether + Zn (78% yield (4)), or abs. alc. (3), or NaOEt (12), or even water (3); from α,β,β,β-tetrachlorodiethyl ether with Zn + abs. alc. (13).]

$\bar{C}$ on warming with conc. H_2SO_4 (14) (2) or on htg. at 150° with conc. HCl (15) or on htg. with benzoic anhydride + a little conc. H_2SO_4 gives (yield 81% (1), 78% (10), 71% (16)) dichloroacetaldehyde (3:5180), b.p. 90–91°.

$\bar{C}$ on htg. with alc. NaOH at 160–180° yields (17) glyoxal tetraethylacetal [Beil. I-760], b.p. 180° (17). — $\bar{C}$ with K *ter*-butylate loses HCl yielding (5) chloroketene diethylacetal, b.p. 166° at 732–740 mm., $D_{15}^{15} = 1.0534$, $n_D^{25} = 1.4375$ (5).

$\bar{C}$ with PCl_5 yields (15) α,β,β-trichlorodiethyl ether [Beil. I-615].

3:6110 (1) van de Walle, *Bull soc. chim. Belg.* **28**, 308–309 (1914/18). (2) Pinner, *Ann.* **179**, 33–34 (1875). (3) Oddo, Mameli, *Gazz. chim ital.* **33**, II 412–414 (1903). (4) Neher, Fleece, *J. Am. Chem. Soc.* **48**, 2422–2423 (1926). (5) Magnani, McElvain, *J. Am. Chem. Soc.* **60**, 2210–2213 (1938). (6) Lieben, *Ann* **104**, 114–115 (1857). (7) I.G., French 814,435, June 23, 1937; *Cent.* **1937**, II 3066, *C A* **32**, 1390 (1938) (8) Ger 528,194, June 26, 1931; *Cent.* **1931**, II 1910. (9) Fritsch, *Ann.* **279**, 300 (1894). (10) [illegible]
(11) Chattaway, Backeberg, *J* [illegible]
(13) Neher, Foster, *J. Am. Che*[illegible]
(15) Krey, *Jahresber.* **1876**, 475. [illegible]
148–151 (1872).

3:6125 *d,l*-α-CHLOROPROPIONIC ACID $C_3H_5O_2Cl$ Beil. II - 248
(2-Chloropropanoic acid) $CH_3—CH.COOH$ (with Cl on CH) II_1-(110) II_2-(226)

B.P. 186° cor.	(1)	$D_4^{20} = 1.2585$ (6)	$n_D^{20} = 1.4350$ (6)
186°	(2)		
185.2° at 760 mm.	(3)		$n_D^{19.4} = 1.4364$ (3)
185°	(4)		
88.6–89.4° at 16 mm.	(3)		
83.5–84.5° at 12 mm.	(5)		

Colorless liq. with weak odor suggestive both of acetic acid and butyric acid; misc. with aq. alc. or ether; volatile with steam; blisters skin.

[For prepn. of $\bar{C}$ from propionic acid (1:1025) with Cl_2 (7) (8) or with SO_2Cl_2 + dibenzoyl peroxide in CCl_4 (9) see indic. refs., from α-chloropropionyl chloride (3:5320) by hydrolysis (1) (10) (11) (12) with water see indic. refs.; from α-chloropropionitrile by hydrolysis with conc. HCl see (5); from 2-chloropropanol-1 (3:7917) (4) or from 3-chlorobutanone-2 (α-chloroethyl methyl ketone) (3:7598) (13) (14) by oxidn. with HNO_3 or other oxidn. agts. see indic. refs.]

[$\bar{C}$ on treatment with Cl_2 as specified (15) yields α,β-dichloropropionic acid (3:0855); $\bar{C}$ with $SOCl_2$ yields (16) α-chloropropionyl chloride (3:5320), b.p. 111°; $\bar{C}$ on reduction with Zn + HCl yields (10) propionic acid (1:1025) [for study of catalytic hydrogenation of $\bar{C}$ or its salts see (17)]; $\bar{C}$ with SO_3 at 170° yields (18) α-chloro-α-sulfopropionic acid [for reactn. of $\bar{C}$ with sulfites see (2)]; $\bar{C}$ with conc. aq. NH_4OH gives (43–46% yield (19)) *d,l*-alanine (α-aminopropionic acid) [for behavior of $\bar{C}$ with liq. NH_3 see (20) (21)].]

$\bar{C}$ on alk. hydrolysis gives (10) (22) lactic acid (1:0400) [for study of rate of hydrolysis of $\bar{C}$ (23) or its sodium salt (24) see indic. refs.].

[$\bar{C}$ on htg. with pyridine at 100° loses CO_2 and yields (25) ethylpyridinium chloride.]

$\bar{C}$ on conversion to salt, treatment with KCN, and subsequent acidification yields (26) methylmalonic acid, m p. 132° (has been used for ident. of $\bar{C}$ (26)).

C̄ with o-phenylenediamine in 5 N HCl refluxed 3 hrs. gives (yields: 61–64% (35), 55–60% (36)) 2 (α-chloroethyl)benzimidazole, ndls. from hot C_6H_6, m.p. 134.7–135.4° cor. (35) 134–135° cor. (36).

—— Methyl α-chloropropionate: b.p. 132°. (See 3:7908.)

—— Ethyl α-chloropropionate: b.p. 147°. (See 3:8125.)

Ⓓ α-Chloropropionamide: m.p. 80° (27). [From ethyl α-chloropropionate (3:8125) with conc. aq. NH_4OH (27).]

Ⓓ α-Chloropropion-anilide: lfts. from lgr., m.p. 92° (28) (9). [From α-chloropropionyl chloride (3:5320) + aniline in $CHCl_3$ (28).] [Note that the reactn. prod. of this compd. with more aniline, viz., α-anilinopropionanilide [Beil. XII-558], has m.p. 126°.]

Ⓓ α-Chloropropion-p-toluidide: lfts. from lgr., m.p. 124° (28), 108° (29). [From α-chloropropionyl chloride (3:5320) with 2 moles p-toluidine (28).] [Note that the reactn. prod. of this compd. with more p-toluidine, viz., α-(p-toluidino)propion-p-toluidide [Beil. XII-980] has m.p. 158°.]

Ⓓ Phenylhydrazine α-chloropropionate: m.p. 95° (30). [From C̄ + phenylhydrazine (30).]

Ⓓ α-Phenoxypropionic acid: ndls. from aq., m.p. 115–116° (31), 115° (32). [From sodium α-chloropropionate + sodium phenolate on htg. and evapn. (33).] [Note that the opt. act. forms of this deriv. melt at 87° (32).]

3:6125 (1) Buchanan, *Ann.* **148**, 170 (1868). (2) Backer, von Mels, *Rec. trav. chim.* **49**, 177–194, 363–380 (1930). (3) Burkard, Kahovec, *Monatsh.* **71**, 340 (1938). (4) Henry, *Bull. acad. roy. Belg.* **1903**, 397–431; *Cent.* **1903**, II 486. (5) Michael, *Ber.* **34**, 4049–4050 (1901). (6) Schjanberg, *Z. physik. Chem.* **A-172**, 230 (1935). (7) Bass, Burlew (to Dow Chem. Co.), U.S. 1,993,713, March 5, 1935; *Cent.* **1935**, II 1257; *C.A.* **29**, 2550 (1935). (8) Bass (to Dow Chem. Co.), U.S. 2,010,685, Aug. 6, 1935; *Cent.* **1936**, I 880; *C.A.* **29**, 6608 (1935). (9) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (10) Ulrich, *Ann.* **109**, 269–271 (1859).

(12) Lovén, *J. prakt. Chem.* (2) **29**, 367 (1884).
U.S. 2,051,470, Aug. 18, 1936; *Cent.* **1936**, II
sche Petrol
ent. **1936**, II
33, II 1587.
31). (18) I
. *Soc.* **59**, 850 (1937). (20) Cheronis, Spitz-
78 (1941). (22) Wichelhaus, *Ann.* **143**, 4–5
(1867). (23) Kailan, Kunze, *Monatsh.* **71**, (1938). (24) Simpson, *J. Am. Chem. Soc.* **40**, 678 (1918). (25) von Walther, Weinhagen, *prakt. Chem.* (2) **96**, 53–54 (1917). (26) Bloomfield, Farmer, *J. Chem. Soc.* **1932**, 2076–207 (27) Beckurts, Otto, *Ber.* **9**, 1592 (1876). (28) Bischoff, Walden, *Ann.* 2 (30)
Stempel, Schaffel, *J. Am.*
(31) Bischoff, *Ber.* **33**, 4) **31**,
992 (1922). (33) Saarba , *Bull.*
soc. chim. Belg. **45**, 255 (19 Roeder, Skolnik,
Miller, Day, *J. Am. Chem. Soc.* **65**, 1856 (1943).

3:6135 n-PROPYL TRICHLOROACETATE $C_5H_7O_2Cl_3$ Beil. II - 209

n-$C_3H_7O.CO.CCl_3$ II_1— II_2—

B.P.			
186.9–187.1° (1)	D_4^{20} = 1.3221 (6)	n_D^{20} = 1.4501	(6)
186.5–187° at 763 mm. (2)	1.3213 (5)	1.4507	(5)
187° (3)	D_4^{15} = 1.3170 (4)	n_D^{15} = 1.4508	(4)
117–117.3° at 130 mm. (1)			
69° at 10 mm. (4)			
65.0–65.5° at 5 mm. (5)			

[For prepn. (57% yield (4)) from n-propyl alc. (1:6150) + trichloroacetic ac. (3:1150) see (4).]

[For study of chlorination of $\bar{C}$ see (4).]

For study of hydrolysis of $\bar{C}$ see (5).

3:6135 (1) Cheng, *Z physik. Chem.* **B-24**, 307 (1934) (2) Schiff, *Z. physik. Chem.* **1**, 379 (1887). (3) Clermont, *Bull soc chim.* (2) **40**, 302 (1883). (4) Gayler, Waddle, *J. Am. Chem. Soc.* **63**, 3358–3359 (1942). (5) Palomaa, Salmi, Korte, *Ber* **72**, 797 (1939). (6) Schjanberg, *Z. physik. Chem.* **A-172**, 229 (1935).

3:6140 ISOBUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. II - 209

$(CH_3)_2CH\ CH_2.O.CO\ CCl_3$ II_1— II_2—

B.P. 187–189° (1)	D_4^{25} = 1.255 (2)	n_D^{25} = 1.4456	(2)
93–94° at 24 mm. (2)	D_4^{20} = 1.2636 (3)	n_D^{20} = 1.4483	(3)

Colorless liq. of agreeable odor (1).

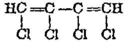
[For prepn. (82–89% yield (2)) from isobutyl alc. (1:6165) + trichloroacetic ac. (3:1150) see (2) (1).]

[For study of chlorination of $\bar{C}$ see (2).]

3:6140 (1) Judson, *Ber.* **3**, 784 (1870). (2) Waddle, Adkins, *J. Am Chem. Soc.* **61**, 3361–3364 (1939). (3) Schjanberg, *Z. physik. Chem.* **A-172**, 229 (1935)

3:6150 1,2,3,4-TETRACHLOROBUTADIENE-1,3 $C_4H_2Cl_4$ Beil. S.N. 12

(Liquid stereoisomer)



B.P. 188° (1)	D_{15}^{15} = 1.516 (1)
67–68° at 10 mm. (1)	
43° at 1 mm. (1)	

[*See also the solid stereoisomer* (3:0870), *m.p.* 50°.]

Colorless strongly refractive liq. with agreeable honey-like odor; on stdg. turns brown and evolves HCl.

[For isolation of $\bar{C}$ from the high-boilg. fractn. resulting in the preparation of trichloroethylene (3:5170) from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) see (1); for prepn. of $\bar{C}$ from 1,1,2,3,4,4-hexachlorobutane (3:3155) with alc. KOH at room temp. see (1).]

$\bar{C}$ on saturation with Cl_2 yields (1) the liquid stereoisomer of 1,1,2,3,4,4-...

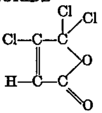
2 (3:9046), b.p. 97° at 10 mm. (1). [Note that $\bar{C}$ does *not* (1) yield octachlorobutane (3:2000).]

$\bar{C}$ with Br_2 yields 1,4-dibromo-1,2,3,4-tetrachlorobutene-2, long colorless doubly refracting ndls., m.p 105° (1).

$\bar{C}$ does not react with conc. HNO_3, but with fumg. HNO_3 or even with NO_2 gas $\bar{C}$ reacts vigorously pptg. 1,4-dinitro-1,2,3,4-tetrachlorobutene-2, colorless cryst. from AcOH, m.p. 131° (1). [Note that this prod. cannot be recryst. from alc. since it reacts yielding ethyl nitrite and a yel. viscous oil (1).]

3:6150 (1) Müller, Huther, *Ber.* **64**, 589–600 (1931); *C.A.* **25**, 3956 (1931).

3:6158 CHLOROMALEYL (DI)CHLORIDE $C_4HO_2Cl_3$ Beil. XVII—XVII$_1$-(138)



B.P.		M.P.					
189.3°	at 760 mm. (1)	**12.7°** (1)	D_4^{20} = **1.602**	(3)	n_D^{20} = **1.5126**	(3)
186.3°	at 760 mm. (1)	**11–12°** (2)				
185.2°	at 730 mm. (1)		$D_4^{18.1}$ = **1.6049**	(3)	$n_D^{18.1}$ = **1.51362**	(3)
104.0–105°	at 50 mm. (2)					
82.2–82.5°	at 26 mm. (3)		$D_4^{17.5}$ = **1.6044**	(3)	$n_D^{17.5}$ = **1.51375**	(3)
71.5°	at 10 mm. (1)					

[*See also chlorofumaryl (di)chloride* (3:6105).]

$\bar{C}$ is generally formulated in the unsymmetrical structure shown above (for discussion see (1) (2)); note, however, that the position of the chlorine atom attached to the carbon bearing the double bond is frankly assumed and may be on the other such carbon.

Note also that $\bar{C}$ appears to exist also in a labile form, m.p. 4.8° (1), which readily changes to the higher-melting (stable) variety; $\bar{C}$ on supercooling and inoculation with the labile form cryst. in the latter.

$\bar{C}$ from pet. ether cryst. as needles; $\bar{C}$ has disagreeable odor (1) and is far more lachrymatory than the isomeric chlorofumaryl (di)chloride (3:6105) (2).

[For prepn. of $\bar{C}$ from chlorofumaryl (di)chloride (3:6105) by combination with $AlCl_3$, htg. at 100° for several hrs., and subsequently decomposing with ice water (yield as high as 85–87% but varies according to nature of $AlCl_3$ used) see (1) (2).]

[$\bar{C}$ on hydrogenation in dry ether in pres. of Pt black yields (4) *n*-butyric acid (1:1035) and other prods.]

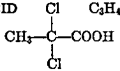
[$\bar{C}$ with $AlCl_3$ gives a cpd., red-brown ndls., m.p. abt. 100° (1); on htg. at 180–225° this prod. decomposes yielding (1) α,β-dichloroacryloyl chloride (see under 3:2265), b.p. 147.3° at 733 mm., phosgene (3:5000), CO, HCl, and other prods.]

$\bar{C}$ on protracted boilg. is converted (1) to chlorofumaryl (di)chloride (3:6105).

[$\bar{C}$ reacts with MeOH and with aniline much more slowly than the isomeric chlorofumaryl (di)chloride (3:6105) (for details and graphs see (1) cf. (2)).]

3:6158 (1) Ott, *Ann.* **392**, 256–265, 278–285 (1912). (2) Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* **1933**, 15–21. (3) von Auwers, Schmidt, *Ber.* **46**, 482 (1913). (4) Ott, *Ber.* **46**, 2173–2175 (1913).

3:6162 α,α-DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ **Beil. II - 250**
II_1—
II_2-(228)



B.P. [185–190°] (1) (4) (6)
186–189° (7)
90–92° at 14 mm. (2)

$D_4^{22.8}$ = **1.389** (2)

Colorless liq. — Very eas. sol. aq. or alc.; from aq. solns. can be salted out with NaCl. — Volatile with steam without hydrolysis — Insol. conc. HCl.

[For prepn. of $\bar{C}$ from corresp. acid chloride, viz., α,α-dichloropropionyl chloride (3:5372), by hydrolysis see (3); from α,α-dichloropropionitrile monomer [Beil. II-251] (1) (4) (19), α,α-dichloropropionitrile dimer [Beil. II-252] (5), or α,α-dichloropropionitrile trimer [Beil. XXVI-38] (6) (7) by hydrolysis with H_2SO_4 see indic. refs.; from α,α-dichloropropionanilide (see below) by hydrolysis with conc. HCl in s t. at 140° see (2); for formn. of $\bar{C}$ from propionic acid with Cl_2 under certain conditions see (26).]

$\bar{C}$ is reduced by Zn + dil. H_2SO_4 giving (1) propionic acid (1:1025).

$\bar{C}$ on keeping gradually splits off some HCl (2). — $\bar{C}$ with alc. KOH on boilg. either loses HCl giving (8) α-chloroacrylic acid (3:1445) or by some obscure mechanism gives (9) cf. (10) (11) β-ethoxyacrylic acid [Beil. III-369], m p. 110°.

$\bar{C}$ as a monobasic acid forms corresp. salts; e.g., $NH_4\bar{A}$ (1), $K\bar{A}.6H_2O$ (1); $Ca\bar{A}_2.3H_2O$ (1); $Ba\bar{A}_2.H_2O$ (1); $Zn\bar{A}_2.H_2O$ (1) (12), $Ag\bar{A}$, spar. sol. aq. (1), note that this dry $Ag\bar{A}$ at 60° decomposes violently giving (12) AgCl and a mixed anhydride of $\bar{C}$ with pyruvic acid, viz., $CH_3.C(Cl_2).CO\ O.CO.CO.CH_3$; however, $Ag\bar{A}$ on warming with aq. gives (12) AgCl + pyruvic acid (1:1040) and/or (1) α-chloroacrylic acid (3:1445).

$\bar{C}$ with aq. Ag_2O or Ag_2CO_3 on protracted htg. gives (13) (12) pyruvic acid (1:1040), but use of excess Ag_2O (14) (1) cf (15) leads to AcOH (1:1010) + CO_2 + H_2O. — $\bar{C}$ with aq. $Ba(OH)_2$ on boilg or $\bar{C}$ with aq. in s.t. at 120–150° gives (14) (16) pyruvic acid (1:1040).

[$\bar{C}$ with finely divided Ag in C_6H_6 on refluxing 40–70 hrs. gives (17) (18) (19) α,α′-dimethylmaleic anhydride [Beil. XVII-445], m.p. 95°, and α,α′-dichloro-α,α′-dimethylsuccinic acid [Beil. II-668], m.p. 185°.]

[$\bar{C}$ (3 moles) with PCl_3 (1 mole) gives (3) (20) α,α-dichloropropionic acid anhydride [Beil. II-251], b.p. 196–200° (20), 190–192° (3). — $\bar{C}$ (3 moles) with PCl_3 (2 moles) (3) or with $SOCl_2$ refluxed for 10 hrs. (21) gives α,α-dichloropropionyl chloride (3:5372).]

$\bar{C}$ with alcohols in pres. of dry HCl gives (1) the corresp. esters (see also below).

—— **Methyl α,α-dichloropropionate:** b.p. 144–146° (7), 143–144 u c. (1). [From $\bar{C}$ with MeOH + dry HCl (1) (7); for study of kinetics of hydrolysis see (22).]

—— **Ethyl α,α-dichloropropionate:** b.p. 160° (23), 156–157° (1) (6), 83–85° at 53 mm. (2). [From $\bar{C}$ with EtOH + dry HCl (1) or from α,α-dichloropropionyl chloride (3:5372) with EtOH (23); note that this ester with aq. in s.t. at 130° gives (16) (14) undergoes hydrolysis yielding pyruvic acid (1:1040) and ethyl pyruvate (1:3308) or with aq. Ag_2O gives (15) Ag acetate]

Ⓓ **α,α-Dichloropropionamide:** lfts. from dil. alc., m.p. 117–118° (2) (24), 117° (12), 116–117° (3), 116° (23) (5) (20), 115–116° (4) (6) (7). [From ethyl α,α-dichloropropionate (above) (3) (23), from methyl α,α-dichloropropionate (above) (7), or from α,α-dichloropropionyl chloride (3:5372) (3) with conc. aq. NH_4OH.]

Ⓓ **α,α-Dichloropropion-N-ethylamide:** m.p. 51–52° (2). [From $\bar{C}$ with $EtNH_2$.]

—— **α,α-Dichloropropionanilide:** m.p. 101° (2). [Reported only by indirect means (2).]

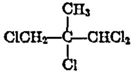
—— **α,α-Dichloropropion-p-toluidide:** m.p. 84–86° (25). [Reported only by indirect means (25).]

3:6162 (1) Beckurts, Otto, *Ber.* **9**, 1876–1881 (1876). (2) von Braun, Jostes, Münch, *Ann.* **453**, 134–135 (1927). (3) Beckurts, Otto, *Ber.* **11**, 386–391 (1878). (4) Beckurts, Otto, *Ber.* **9**, 1593–1594 (1876). (5) Tröger, *J. prakt. Chem.* (2) **46**, 362–363 (1892). (6) Beckurts, Otto, *Ber.* **10**, 263–264 (1877). (7) Otto, Voigt, *J. prakt. Chem.* (2) **36**, 84–85 (1887). (8) Otto, Beckurts, *Ber.* **18**, 241–242 (1885). (9) Otto, *Ber.* **23**, 1108–1110 (1890). (10) Claisen, *Ber.* **31**, 1020 (1898).

(11) Tschitschibabin, *J. prakt. Chem.* (2) **73**, 335 (1906). (12) Beckurts, Otto, *Ber.* **18**, 228–235 (1885). (13) Beckurts, Otto, *Ber.* **10**, 265–266 (1877). (14) Beckurts, Otto, *Ber.* **10**, 2037–2039 (1877). (15) Klimenko, *Ber.* **7**, 1405–1406 (1874). (16) Klimenko, *Ber.* **5**, 477 (1872). (17) Beckurts, Otto, *Ber* **10**, 1503–1504 (1877). (18) Otto, Beckurts, *Ber.* **18**, 826–830, 836, 847 (1885). (19) Otto, Holst, *J. prakt. Chem.* (2) **41**, 461–467 (1890). (20) Otto, Holst, *J. prakt. Chem.* (2) **42**, 78 (1890).

(21) Leimu, *Ber.* **70**, 1050 (1937). (22) Burki, *Helv. Chim. Acta* **1**, 244–245 (1918). (23) Klimenko, *Ber.* **3**, 466–467 (1870). (24) Otto, *Ann.* **132**, 183 (1864). (25) Bischoff, Walden, *Ann.* **279**, 93 (1894) (26) Röhm and Haas, A.G., Ger. 579,654, June 29, 1933; *Cent.* **1933** II 1587; [*C.A.* **28**, 1056 (1934)].

3:6165 1,1,2,3-TETRACHLORO-2-METHYLPROPANE $C_4H_6Cl_4$ Beil. S.N. 10



B.P.	M.P.		
190.6–191.3° cor. (1)	**−46°** (1)	D_4^{25} = **1.4393** (1)	n_D^{20} = **1.4963** (1)

[For formn. of C̄ (together with other products) from *ter*-butyl chloride (3:7045) or from 1,3-dichloro-2-methylpropane (3:7960) + Cl_2 see (1).]

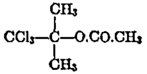
3:6165 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1027–1029 (1936).

3:6180 β,β,β-TRICHLORO-*ter*-BUTYL ACETATE $C_6H_9O_2Cl_3$ Beil. II - 131

("Acetone-chloroform" acetate; "chloretone" acetate)

II₁- (50)

II₂—



B.P. **191°** (1)
190–191° (2)
151–152° at **237** mm. (3)

Colorless mobile liq. with agreeable odor (1). Insol. aq.; eas. sol. alc., ether, acetone, $CHCl_3$, C_6H_6 (3). — Volatile with steam (3).

C̄ on boilg. with 3–4 vols. conc. HNO_3 is rapidly hydrolyzed; after boilg. only a few min. addn. of aq. ppts. β,β,β-trichloro-*ter*-butyl alc. (3:2662), m.p. 78° (3). [C̄ hydrolyzes only very slowly (108 hrs.) on boilg. with aq. alone; in pres. of dil. H_2SO_4 hydrolysis is more rapid (7 hrs.) and β,β,β-trichloro-*ter*-butyl alc. (chloretone) sublimes into condenser (3).]

[For prepn. from β,β,β-trichloro-*ter*-butyl alc. (3:2662) + Ac_2O (1) or Ac_2O + NaOAc (3) see (1) (3).]

3:6180 (1) Willgerodt, Dürr, *J. prakt. Chem.* (2) **39**, 285 (1889). (2) Taffe, *Roczniki Farm.* **2**, 99–107 (1923); *Cent.* **1924**, II 304. (3) Aldrich, *J. Am. Chem. Soc.* **37**, 2720–2723 (1915).

3:6185 ***ter*-AMYL TRICHLOROACETATE** $C_7H_{11}O_2Cl_3$ **Beil. S.N. 160**

$$CH_3CH_2.\overset{CH_3}{\underset{CH_3}{C}}.O.CO.CCl_3$$

B.P. 191° at 756 mm. (1) D_{20}^{20} **= 1.2505 (1)**
105° at 30 mm. (1)

C̄ on distn. tends to decompose into 2-methylbutene-2 (1:8220) + trichloroacetic acid (3:1150) (1).

[For studies on prepn. from 2-methylbutene-2 (1:8220) + trichloroacetic acid (3:1150) see (2) (3) (4) (5) (6); for prepn. (84% yield (1)) from *ter*-amyl alc. (1:6160) and trichloroacetic ac. (3:1150) see (1).]

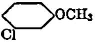
3:6185 (1) Liston, Dehn, *J. Am. Chem. Soc.* **60**, 1264–1265 (1938). (2) Timofeev, Andreasov, *J. chim. Ukraine* **1**, 107–110 (1925); *C.A.* **20**, 2820 (1926). (3) Timofeev, Israilevich, Chashes, [illegible] *em. Zhur.* [illegible] *, Ukrain.* [illegible] ndreasov, [illegible]

—— TRICHLOROMETHYL TRICHLOROACETATE $Cl_3C.COOCCl_3$ **Beil. III - 17**
III_1—
III_2—

B.P. 191–192° **M.P. 34°** D_4^{35} **= 1.67331**

See 3:0290. *Division A: Solids.*

3:6195 ***m*-CHLOROANISOLE** (*m*-Chlorophenyl methyl ether) C_7H_7OCl **Beil. VI - 185** **VI_1-(100)**



B.P.

193–194°	**(1)**	$D_4^{12.0}$ **= 1.1759 (4)**	$n_{He}^{12.0}$ **= 1.53783 (4)**
193°	***(2)***		
191–192° at 728 mm.	**(3)**		

Oil. — Volatile with steam (3). — Odor like anisole (5). — Sol. alc., ether.

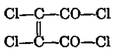
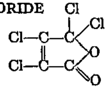
[For prepn. of C̄ from *m*-chlorophenol (3:0255) by htg. with KOH + MeI in MeOH (1) or Me_2SO_4 + alk. (7) see (1) (7); from *m*-chloroaniline by diazotization and warming with MeOH see (2); from *m*-aminophenyl methyl ether by diazotization and reactn. with CuCl see (3).]

C̄ on nitration with 1 pt. fumg. HNO_3 ($D = 1.52$) at −10 to +25° yields (6) a product, m.p. 81° (6), which may have been an impure form of the trinitro cpd., 2,4,6-trinitro-3-chloroanisole, m.p. 86°, obtd. (61% yield (7)) by use of 5 pts. fumg. HNO_3 ($D = 1.51$) + 5 pts. conc. H_2SO_4 at −15°. [The numerous possible mono- and di-nitration products of C̄ cannot be discussed here and, in any case, have not been reported by direct nitration of C̄.]

[For a study of the reactn. kinetics of the splitting of C̄ in acid soln. see (8).]

3:6195 (1) Gattermann, *Ann.* **357**, 319 (1907). (2) Cameron, *Am. Chem. J.* **20**, 238 (1898). (3) Reverdin, Eckhard, *Ber.* **32**, 2626 (1899). (4) von Auwers, *Z. physik. Chem.* **A-158**, 418 (1932). (5) Holleman, *Rec. trav. chim.* **37**, 104 (1918). (6) Reverdin, Phillip, *Ber.* **38**, 3776 (1905); *Bull. soc. chim.* (3) **33**, 1322 (1905). (7) Schlubach, Mergenthaler, *Ber.* **58**, 2734 (1925). (8) Ghaswalla, Donnan, *J. Chem. Soc.* **1936**, 1341–1346.

3:6197 DICHLOROMALEYL (DI)CHLORIDE $C_4O_2Cl_4$ Beil. II - 754 XVII$_1$-(138)

 and/ or 

sym. form (A) *unsym.* form (B)

B.P.			
192–194°	(1)	*unsym.* (B) D_4^{20} = 1.7091 (2)	n_{He}^{20} = 1.51947 (2)
190° at 743 mm.	(2)		
86–89° at 11 mm.	(3)	*sym.* (A) D_4^{20} = 1.6723 (2)	n_{He}^{20} = 1.51572 (2)

[*See also dichloromaleic acid* (3:3634) *and dichloromaleic anhydride* (3:3635).]

Colorless mobile lachrymatory liq. with penetrating camphoraceous odor but *not* fumg. in moist air. — Insol. aq. but volatile with steam without hydrolysis. — Soluble in org. solvents.

Although C̄ has not been separated into the completely pure desmotropic forms (A) and (B), their presence is clearly evidenced (2). The relative proportion of the two forms varies with the age of the sample and other conditions, but the above data on density and refraction indicate the extremes so far realized (for much further detail see (2)).

[For prepn. of ord. C̄ (mixt. of (A) and (B)) from succinyl (di)chloride (3:6200) with Cl_2 at 145° in pres. of Fe (81% yield) see (2) (note that some dichloromaleic anhydride (3:3635) is also formed, that in absence of Fe the reactn. is very slow, and that use of I_2 in place of Fe lowers yield of C̄ to 54% (2)); from chlorofumaryl (di)chloride (3:6105) with Cl_2 in pres. of Fe see (1); from dichloromaleic anhydride (3:3635) with PCl_5 see (1); from dibromofumaryl (di)chloride [Beil. II$_1$-(303)] with $AlCl_3$ at 100° see (3).]

Ord. C̄ with 60% of its wt. of $AlCl_3$ spontaneously evolves ht.; after further htg. at 100° and pouring into aq. the ethereal extract yields (2) a prod. which reacts as substantially pure *unsym.* form (B).

Ord. C̄ is not affected by ord. treatment with boilg. aq. or boilg. aq. KOH (2), although it is attacked by alc. KOH (1). — C̄ on very protracted (168 hrs.) boilg. with aq. slowly dissolves giving (2) an acidic soln. which on extraction with ether followed by drying and evapn. of this solvent gives (80% yield) dichloromaleic anhydride (3:3635).

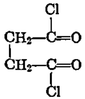
[For study of rate of reactn. of C̄ with MeOH or with aniline see (2).]

[For condens. of C̄ with 1-aminoanthraquinone in prepn. of dyestuffs see (2) (4).]

Ord. C̄ (2 g.) in C_6H_6 (150 ml.) treated with 4 moles aniline (3.4 g.) in C_6H_6 (30 ml.) immediately ppts. aniline hydrochloride; after stdg for ½ hr., then removing this ppt., the filtrate leaves on evapn. a mixt. (m.p. 165–185°; yield 67–83% (2)) of two different dianilides, which can be separated by recrystn. from hot alc.: the dianilide from the *sym.* dichloride (A) is *white*, has m.p. 193°, and with alc. KOH is much more slowly hydrolyzed than its isomer and during such hydrolysis shows no transient color; the dianilide from the *unsym.* dichloride (B) is *yellow*, has m.p. 170°, and with hot 8% alc. KOH readily hydrolyzes with development of a transient cherry-red coloration. — Note that, although the *white* dianilide is somewhat more readily sol. in hot alc. than the *yellow* isomer, it also separates first on slow cooling; note also that on hydrolysis of the anilides with alc. KOH the presence of aniline is readily detected but (presumably because of further attack by the alkali) no dichloromaleic acid can be recovered in either case.

3:6197 (1) Vandevelde, *Bull. acad. roy. Belg.* (3) **37**, 680–700 (1899); *Cent.* **1900**, I 404. (2) Leder, *J. prakt. Chem.* (2) **130**, 255–288 (1931). (3) Ott, *Ann.* **392**, 271 (1912). (4) Leder, Ger. 558,248, Sept. 3, 1932; *Cent.* **1932**, II 3789.

3:6200 SUCCINYL (DI)CHLORIDE $C_4H_4O_2Cl_2$ Beil. II - 613
II₁-(264)
II₂-(553)



B.P.			M.P.		
193.3°	at 760 mm.	(1)	20°	(7)	D_4^{20} = 1.3748 (9) n_D^{20} = 1.4683 (9)
190–192° cor.	at 760 mm.	(2)	18.5°	(5)	
150–152° cor.	at 214 mm.	(2)	17.7°	(9)	$D_4^{15.2}$ = 1.3948 (6) $n_D^{15.2}$ = 1.47348 (6)
114–116°	at 55 mm.	(3)	17°	(10)	
103–104°	at 25 mm.	(4)	16–17°	(4)	
95° cor.	at 20 mm.	(5)			
88.8°	at 19 mm.	(6)			
87–88°	at 18 mm.	(7)			
95–96°	at 16 mm.	(19)			
103°	at 15 mm.	(8)			
78.6°	at 11 mm.	(9)			

Note that $\bar{C}$ may react in either *sym.* (above) or *unsym.* form acc. to circumstances. [For discussion of structure see (1) (5) (7) (9) (10); in the liquid only the *sym* form ($\bar{C}$) exists (9).] — $\bar{C}$ is sol. in C_6H_6, but insol in pet. ether (7)

[For prepn. of $\bar{C}$ from succinic acid (1.0530) with PCl_5 (yield: 85% (8) (12)) (13) (14) (4) (5) see indic. refs (note that neither $PCl_3 + ZnCl_2$ (8) nor $SOCl_2$ (16) give $\bar{C}$); for prepn of $\bar{C}$ from succinic anhydride (1.0710) with PCl_5 (4) (6), with $PCl_3 + Cl_2$ (17), or with $SOCl_2 + ZnCl_2$ at 200–240° (18) (35) see indic. refs.; for formn. of $\bar{C}$ from the trimer of β-aldehydopropionic acid with PCl_5 see (19)]

[$\bar{C}$ with Cl_2 + Fe at 145° gives (81% yield (20)) dichloromaleyl dichloride (3·6197) cf. (21), $\bar{C}$ with Br_2 yields (22) (23) mixt of *d,l*- and *meso-α,α'*-dibromosuccinyl dichlorides; $\bar{C}$ with Br_2 + Fe yields (24) dibromomaleic anhydride [Beil. XVII-435, XVII₁-(233)], m.p. 118°.]

[$\bar{C}$ on reduction with Na/Hg + AcOH in ether (25) or with H_2 + Pd (26) (15) gives (54% yield (26)) γ-butyrolactone (1:5070), b.p. 206°.]

[$\bar{C}$ with $AlCl_3 + C_6H_6$ yields (27) γ,γ-diphenyl-γ-butyrolactone [Beil. XVII-367], m p. 90° (arising from reactn of $\bar{C}$ in the *unsym* form), 1,2-dibenzoylethane [Beil. VII-773, VII₁-(401)], m p. 144° (arising from reactn. of the *sym.* form), and β-benzoylpropionic acid [Beil X-696, X₁-(330)], m.p. 116°.]

[$\bar{C}$ on distn. or htg. with succinic acid (1.0530) (30) (31), or on htg. (31) with anhydrous oxalic acid (1:0535) or on protracted boiling with Na in xylene (32), or on htg. with diethyl succinate (1:3756) + $ZnCl_2$ (33), yields succinic anhydride (1:0710), m p. 120°.]

$\bar{C}$ with conc. aq. NH_4OH (7) or with NH_3 gas in C_6H_6 reacts mainly in the *unsym.* form (7) yielding the hygroscopic *unsym.* succindiamide [Beil XVII-410] with at most 5% of *sym*-succindiamide, m.p 260°; $\bar{C}$ with aniline in C_6H_6 (7) (34), however, gives 90% yield (7) *sym*-succindianilide, m p. 230°.

[For behavior of $\bar{C}$ with diethyl sodio-malonate see (35) (36).]

$\bar{C}$ on hydrolysis yields succinic acid (1:0530) q.v., m p. 185°.

3:6200 (1) Ott, *Ann.* **392**, 277 (1912). (2) Perkin, *J. Chem. Soc.* **53**, 563–564 (1888). (3) Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* **1933**, 18. (4) Vorländer, *Ann.* **280**, 183–184

(1894). (5) Garner, Sugden, *J. Chem. Soc.* **1927**, 2878–2880. (6) von Auwers, Schmidt, *Ber.* **46**, 478 (1913). (7) Morrell, *J. Chem. Soc.* **105**, 1736–1739 (1914). (8) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (9) Martin, Partington, *J. Chem. Soc.* **1936**, 1170–1181. (10) Purvis, Jones, Tasker, *J. Chem. Soc.* **97**, 2289 (1910).

(11) Vorländer, *Ber.* **30**, 2268–2269, Note (1897). (12) Curtius, Hechtenberg, *J. prakt. Chem.* (2) **105**, 302, Note (1923). (13) Gerhardt, Chiozza, *Ann.* **87**, 293–294 (1853). (14) Möller, *J. prakt. Chem.* (2) **22**, 208 (1880). (15) Fröschl, Maier, *Monatsh.* **59**, 264–268 (1932). (16) McMaster, Ahmann, *J. Am. Chem. Soc.* **50**, 146 (1928). (17) Clemmensen, Miller (to Monsanto Chemical Co.), U.S. 1,974,845, Sept. 25, 1934; *Cent.* **1935**, I 960; *C.A.* **28**, 7265 (1934). (18) Kyrides (to Monsanto Chem. Co.), U.S. 1,951,304, March 20, 1934; *Cent.* **1934**, II 333. (19) Carrière, *Ann. chim.* (9) **17**, 91 (1922). (20) Leder, *J. prakt. Chem.* (2) **130**, 269–271 (1931).

(21) Kauder, *J. prakt. Chem.* (2) **31**, 1–36 (1895). (22) Ing, Perkin, *J. Chem. Soc.* **125**, 1815, 1822 (1924). (23 [illegible]
37, 680–700; *Cent.* [illegible]
J. prakt. Chem. (2) [illegible]
Ann. **526**, 17 (19[illegible]
315–318 (1888).

(31) Anschütz, *Ann.* **226**, 6, 16–17 (1884). (32) Pearl, Evans, Dehn, *J. Am. Chem. Soc.* **60**, 2470 (1938). (33) Kyrides, Dvornikoff, *J. Am. Chem. Soc.* **55**, 4630 (1933). (34) Dunlap, Cummer, *J. Am. Chem. Soc.* **25**, 621 (1903). (35) Ruggli, Maeder, *Helv. Chim. Acta* **26**, 1476–1498 (1943); *C.A.* **38**, 2934 (1944). (36) Ruggli, Maeder, *Helv. Chim. Acta* **26**, 1499–1511 (1943); *C.A.* **38**, 2935 (1944).

3:6205 PENTACHLOROPROPANONE-2 C_3HOCl_5 Beil. I - 656

(Pentachloroacetone) $Cl_2CH-\underset{\underset{O}{\|}}{C}-CCl_3$ I_1— I_2—

B.P.		F.P.		
192°	at 753 mm. (1)	**+2.1°** (2)	D^{15}_{15} = **1.69**	(3)
97.5–98.5° at 40 mm.	(2)		D^{14}_{-} = **1.576**	(1)

[*See also hexachloropropanone*-2 (3:6312).]

Colorless oil with odor suggesting chloral (3:5210); slightly sol. cold aq. (aq. at 0° dis. 0.1 vol. C̄ (1)) but on warming to 50–60° the soln. becomes turbid. — C̄ with aq. at 0° forms (1) (4) a crystn. tetrahydrate, m.p. 15–17° (4), 15° dec. (1). — C̄ is volatile with steam.

[For prepn. of C̄ from acetone (1:5400) with Cl_2 in sunlight see (1); from chloroacetone (3:5425) with Cl_2 at 50–70° in light see (5) cf. (3); from citric acid (1:0455) in aq. soln. at 100° with Cl_2 see (1); from chloranilic acid (3:4970) in aq. with Cl_2 in pres. of I_2 see (6); from isopropyl alcohol (1:6135) at 65° with Cl_2 see (7); for formn. of C̄ from citric acid, gallic acid, quinic acid, salicylic acid, indigo, etc., by distn. with HCl + $KClO_3$ see (4); note that in prepn. of C̄ some hexachloroacetone (3:6312) is frequently also obtd.]

C̄ with PCl_5 in s.t. at 180° for 6–8 hrs. yields (8) 1,1,1,2,2,3,3-heptachloropropane (3:0200) b.p. 247–248°, m.p. 30°.

C̄ with dil. aq. KOH undergoes hydrolytic cleavage yielding (1) (3) chloroform (3:5050) and the K salt of dichloroacetic acid (3:6208).

C̄ with aniline in dil. AcOH yields (1) (3) chloroform (3:5050) and dichloroacetanilide [Beil. XII-244, XII_1-(193)], cryst. from aq., C_6H_6, or ether/alc., m.p. 117°. — C̄ with alc. NH_4OH yields (1) chloroform (3:5050) and dichloroacetamide [Beil. II-205, II_1-(92), II_2-(196)], cryst., m.p. 98°.

3:6205 (1) Cloëz, *Ann. chim.* (6) **9**, 187–194 (1886). (2) Edwards, Evans, Watson, *J. Chem. Soc.* **1937**, 1944–1945. (3) Fritsch, *Ber.* **26**, 598 (1893); *Ann.* **279**, 317–318 (1894). (4) Städeler, *Ann.* **11**, 293–301 (1859). (5) I.G., French 816,956, Aug. 21, 1937; *Cent.* **1938**, I 2216. (6) Levy, Jedlicka, *Ann.* **249**, 87–89 (1888). (7) Buc (to Standard Oil Co. of N.J.), U.S. 1,391,757, Sept. 27, 1921; *Cent.* **1922**, IV 942. (8) Fritsch, *Ann.* **297**, 314 (1897).

3:6207 ETHYL α-CHLOROACETOACETATE $C_6H_9O_3Cl$ Beil. III - 662
(Ethyl α-chloro-β-keto-*n*-butyrate) $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{Cl}{|}}{CH}-COOC_2H_5$ III_1-(233) III_2-(426)

B.P. 193°	at	760 mm.	(1)
194°			(9)
193–195°			(2) (10) (15)
197°	at	748 mm.	(3)
188–189°			(4)
108–110°	at	20–26 mm.	(5) (12)
105–110°	at	30 mm.	(6)
86–89°	at	12 mm.	(7)
88–89°	at	11 mm.	(1)
58°	at	2.5 mm.	(3)

[*See also ethyl γ-chloroacetoacetate* (3:6375).]

Colorless oil with penetrating odor; vapor is strong lachrymator. — $\bar{C}$ can be preserved for some time but on very long stdg. (several years) decomposes (8) with formn. of oxalic acid (1:0445). — $\bar{C}$ is spar sol. aq., eas. sol. alc., ether.

[For prepn. of $\bar{C}$ from ethyl acetoacetate (1·1710) with SO_2Cl_2 (yields: 85% (7), 55% (6)) (2) or with Cl_2 in diffused light at room temp. (75% yield (9)) or in gas phase at 76–102° and 7 mm. press. (68% yield (40)) see indic refs.; from the copper enolate of ethyl acetoacetate in $CHCl_3$ with Cl_2 (67% yield (10)) cf. (11); from ethyl sodioacetoacetate with *p*-toluenesulfonyl chloride in dry ether or lgr. (12), or from ethyl β-(chlorimino)-*n*-butyrate [Beil. III-656] on distillation with dil H_2SO_4 (13) see indic. refs.]

[$\bar{C}$ can be further chlorinated e.g., $\bar{C}$ (1 mole) with SO_2Cl_2 (1 mole) gives (1) (2) ethyl α,α-dichloroacetoacetate [Beil. III-663, III_1-(233), III_2-(427)], b.p. 205–207° at 726 mm., 91° at 11 mm. (1), $D_{17.5}^{19} = 1.293$ (14), $n_D^{17} = 1.4492$ (1).]

$\bar{C}$ on hydrolysis with boilg. dil. H_2SO_4 *undergoes ketonic splitting yielding* (15) *chloro*acetone (3:5425) + CO_2 + EtOH (note that this does not distinguish $\bar{C}$ from ethyl γ-chloro-acetoacetate (3:6375) which yields same prods.)

[$\bar{C}$ with alc. $NaOC_2H_5$ yields (9) ethyl acetate (1·3015), ethyl α-ethoxyacetoacetate, and traces of ethyl chloroacetate (3:5700); $\bar{C}$ with sodium phenolate (free from alc. or aq.) on htg. gives (16) ethyl α-phenoxyacetoacetate (not further described) which in cold conc. H_2SO_4 *loses* H_2O *and ring-closes to 2-carbethoxy-3-methylcoumarone* [Beil. XVIII-309], tbls. from C_6H_6, m.p. 51°, b.p. 290° (16); note dif. in behavior of $\bar{C}$ with these reagents as compared with ethyl γ-chloroacetoacetate (3:6375).]

[$\bar{C}$ with diethyl sodiomalonate yields in alc. (7) ethyl acetate (1:3015), ethyl chloroacetate (3:5700), triethyl ethane-1,1,2-tricarboxylate [Beil. II-813, II_1-(321), II_2-(681)], and tetraethyl propane-1,2,2,3-tetracarboxylate [Beil. II-862, II_1-(333), II_2-(701)] but in toluene yields (7) triethyl 3-hydroxybuten-2-tricarboxylate-1,1,2 [Beil. III_2-(509)]; note dif. from behavior of ethyl γ-chloroacetoacetate (3:6375).]

[For behavior of $\bar{C}$ with KCN see (4); with ethyl sodiocyanoacetate see (17); with NH_3 in dry ether see (18).]

Note that $\bar{C}$ is capable of displaying keto enol tautomerism as is shown in the following reactions.

$\bar{C}$ with $FeCl_3$ soln. gives intense violet coloration (10) (4).

$\bar{C}$ [illegible]

alm. ident. with corresp. deriv. from the isomeric ethyl γ-chloroacetoacetate (3:6375)); for corresp. Mg, Cu, or Ni enolates see (20).

[$\bar{C}$ with phenols in pres. of conc. H_2SO_4 or P_2O_5 undergoes condensation and ring closure with loss of H_2O giving the corresp. substituted coumarins: e.g., $\bar{C}$ with *m*-cresol (1:1730) in conc. H_2SO_4 at 0° gives (6) 3-chloro-4,7-dimethylcoumarin, ndls. from alc., m.p. 135° (6); $\bar{C}$ with *p*-cresol (1:1410) similarly (6) (or in small yield (21) with P_2O_5) gives 3-chloro-4,6-dimethylcoumarin, ndls. from AcOH, m.p. 160° (6), 158° (21): for corresp. reactn. of $\bar{C}$ with α-naphthol (1:1500) (22) (6), with β-naphthol (1:1540) (23), with 6-chloro-*m*-cresol (4-chloro-3-methylphenol) (3:1535) (24) see indic. refs. — This type of condensation also occurs with polyhydric phenols: e.g., $\bar{C}$ with resorcinol (1:1530) + conc. H_2SO_4 at 0° (25) or with P_2O_5 in alc. (26) gives 3-chloro-7-hydroxy-4-methylcoumarin, cryst. from alc. with ½ H_2O (lost at 105–110°) and then melting 236° (25) (26); for corresp. behavior of $\bar{C}$ with orcinol (1:1525) (22) (25), with pyrogallol (1:1555) (22) (25), see indic. refs.; many other cases are known. — Note, however, with particular care that $\bar{C}$ with sodium salts of these phenols reacts in a different manner yielding substituted coumarone derivs. (cf. case of sodium phenolate in fifth paragraph).]

$\bar{C}$ with aq. solns. of diazonium salts behaves quite differently from the isomeric ethyl γ-chloroacetoacetate (3:6375): e.g., $\bar{C}$ in alc. with aq. benzenediazonium sulfate in pres of NaOAc (2 moles) yields (27) (28) (4) ethyl α-chloro-α-(phenylhydrazono)acetate [Beil. XV-270], yel. lfts. or pl. from alc., m.p. 80–81° (28) (4), 70–71° (27) (for use of this reactn. on mixts. of $\bar{C}$ with the isomer see (4)).

$\bar{C}$ with excess hydrazine hydrate is reduced with evolution of N_2 (1); $\bar{C}$ with phenylhydrazine (2 moles) condenses and ring-closes yielding (29) (30) 4-(benzeneazo)-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, $XXIV_1$-(319)], or.-red. ndls. from alc., AcOH, or $CHCl_3$, m.p. 156–157° (note, however, that in pres. of ether the reactn. with phenylhydrazine takes a different course yielding (31) ethyl β-(benzeneazo)-crotonate [Beil. XVI-27], red ndls. from alc., m.p. 50–51°).

[$\bar{C}$ with thioacetamide on warming yields (32) 5-carbethoxy-2,4-dimethylthiazole [Beil. XXVII-318], cryst. from ether, m.p. 50–51° (32). — $\bar{C}$ with NH_4SCN (33) or better $Ba(SCN)_2$ (34) in alc. gives (55% yield (34)) 5-carbethoxy-2-hydroxy-4-methylthiazole [Beil. XXVII-338], lfts. from alc., m.p. 128° (33), 127–129° (34); note that this prod. may be regarded as merely the isomeric ethyl α-(thiocyano)acetoacetate (35). — $\bar{C}$ with NH_4 dithiocarbamate (from $NH_4OH + CS_2$) in alc. eliminates NH_4Cl giving an intermediate, m.p. 115–121°, according to mode of htg. (38) but which on fusion ring-closes with loss of aq. to 5-carbethoxy-2-mercapto-4-methylthiazole [Beil. XXVII-339], ndls. from alc., m.p. 150° (38), 141° (39).]

[$\bar{C}$ with urea in alc. contg. a little aq. HCl gives on stdg. 5 months (36) 5-carbethoxy-2-hydroxy-4-methylimidazole [Beil. XXV-216], ndls. from aq. or tbls. from alc., m.p. 218° (36). — $\bar{C}$ (1 mole) with thiourea (1 mole) at 90° reacts vigorously eliminating H_2O and giving (alm. quant. yield (37)) as the hydrochloride 2-amino-5-carbethoxy-4-methylthiazole [Beil. XXVII-338]; addn. of alk. sets free the base, ndls. from ether/alc., m.p. 175° (37) (13).]

3:6207 (1) Macbeth, *J. Chem. Soc.* **123**, 1125 (1923). (2) Allihn, *Ber.* **11**, 567–570 (1878). (3) Milone, *Gazz. chim. ital.* **65**, 342 (1935). (4) Favrel, Prevost, *Bull. soc. chim.* (4) **49**, 243–261 (1931). (5) Haller, Held, *Bull. soc. chim.* (2) **65**, 888–892 (1887). (6) Dey, *J. Chem. Soc.* **107**, 1646 (1915). (7) Gault, Klecs, *Bull. soc. chim.* (4) **39**, 889–905 (1926); *Compt. rend.* **179**, 600 (1924). (8) von Konek-Norwall, *Ber.* **51**, 393–398 (1918). (9) Mewes, *Ann.* **245**, 58–60, 66–69 (18[illegible]) [illegible]). [illegible] –364 (1936). (12) von Meyer, von Findeisen, *J.* [illegible] arend, Schreiber, *Ann.* **318**, 381 (1901). (14) Co [illegible] *Gazz. chim ital.* **22**, II 40–41 (1892). (16) H [illegible] sagne, *Bull. soc. chim.* (4) **1**, 914–916 (1907).

(18) Genvresse, *Ann. chim.* (6) **24**, 64–65 (1891). (19) Wislicenus, Stoeber, *Ber.* **35**, 542–543 (1902). (20) Allihn, *Ber.* **12**, 1298–1300 (1879).

(21) Robertson, Sandrock, *J. Chem. Soc.* **1932**, 1180, 1183–1184. (22) Chakravarti, *J. Indian Chem. Soc.* **8**, 407–411 (1931). (23) Dey, *J. Chem. Soc.* **107**, 1629 (1915). (24) Dey, Dalal, *J. Chem. Soc.* **123**, 3390 (1923). (25) von Pechmann, Hanke, *Ber.* **34**, 357–360 (1901). (26) Chakravarti, *J. Indian Chem. Soc.* **8**, 136 (1931) (27) Bowack, Lapworth, *J. Chem. Soc.* **87**, 1859 (1905). (28) Favrel, *Compt. rend.* **134**, 1313 (1902) (29) Schönbrodt, *Ann.* **253**, 188–193 (1889) (30) Buchka, Sprague, *Ber.* **22**, 2548–2550 (1889).

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3:6208 DICHLOROACETIC ACID

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Cl
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HC—COOH
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Cl
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$C_2H_2O_2Cl_2$

Beil. II - 202
II_1-(90)
II_2-(194)

B.P.		M.P.			
195°	(1) (62)	13.25°	(17)	D_4^{25} = 1.5579 (28)	
194.5–195°	(2)	13.00°	(18)		
194.42° at 760 mm.	(3)	12.15°	(17)	D_{25}^{25} = 1.5604 (4)	
194.0–194.5° cor.	(4)	11°	(19) (20)		
194°	(5) (6)	10.85°	(21)	D_{22}^{22} = 1.5594 (14)	n_D^{22} = 1.4659 (8)
193.5–193.9°	(7)	10.8°	(22)		
192.5° at 763 mm.	(28)	10°	(23) (28)	D_4^{20} = 1.5648 (28) 1.5642 (27)	n_D^{20} = 1.46582 (27)
192–193° cor., dec.	(8)	9.7°	(24) (25)	1.5634 (8)	
191° at 760 mm.	(9)	5–6°	(14)		
190°	(10)	−4.1°	(24)	D_{20}^{20} = 1.5666 (8)	
189–191°	(11)	−4°	(26)		
		See Note 2.		D_4^{19} = 1.5691 (29)	n_D^{19} = 1.4667 (29)
				D_4^{15} = 1.5717 (28)	
				D_{15}^{15} = 1.5707 (27)	
144° at 164 mm.	(12)			See Note 3.	See Note 3.
140° at 142 mm.	(12)				
129° at 88 mm.	(12)				
125° at 71 mm.	(12)				
111.5° at 36 mm.	(12)				
105° at 25 mm.	(13)				
102.5° at 24 mm.	(12)				
99° at 21 mm.	(12)				
102° cor. at 20 mm.	(8) (14)				
102° u.c. at 20 mm.	(16)				
95–96° at 17 mm.	(8)				
91–92° at 12 mm.	(15)				
See Note 1.					

Note 1. The b.p. of Č at normal press. is not very significant, some decompn to dichloroacetyl chloride (3:5290), phosgene (3:5000), and tarry products always occurring (8).

Note 2. Č apparently can exist in at least two crystn. modifications (24); no clear-cut study of the matter, however, has been reported.

Note 3. For values of D_{20}^{20} and n_D^{20} for aq. solns. of Č see (27).

[*See also chloroacetic acid* (3:1370) *and trichloroacetic acid* (3:1150).]

Č when pure is a colorless liq. which does not fume in moist air and which dissolves in

alm. ident. with corresp. deriv. from the isomeric ethyl γ-chloroacetoacetate (3:6375)); for corresp. Mg, Cu, or Ni enolates see (20).

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C̄ with excess hydrazine hydrate is reduced with evolution of N_2 (1); C̄ with phenylhydrazine (2 moles) condenses and ring-closes yielding (29) (30) 4-(benzeneazo)-3-methyl-1-phenylpyrazolone-5 [Beil. XXIV-328, $XXIV_1$-(319)], or.-red. ndls. from alc., AcOH, or $CHCl_3$, m.p. 156–157° (note, however, that in pres. of ether the reactn. with phenylhydrazine takes a different course yielding (31) ethyl β-(benzeneazo)-crotonate [Beil. XVI-27], red ndls. from alc., m.p. 50–51°).

[C̄ with thioacetamide on warming yields (32) 5-carbethoxy-2,4-dimethylthiazole [Beil. XXVII-318], cryst. from ether, m.p. 50–51° (32). — C̄ with NH_4SCN (33) or better Ba-$(SCN)_2$ (34) in alc. gives (55% yield (34)) 5-carbethoxy-2-hydroxy-4-methylthiazole [Beil. XXVII-338], lfts. from alc., m.p. 128° (33), 127–129° (34); note that this prod. may be regarded as merely the isomeric ethyl α-(thiocyano)acetoacetate (35). — C̄ with NH_4 dithiocarbamate (from NH_4OH + CS_2) in alc. eliminates NH_4Cl giving an intermediate, m.p. 115–121°, according to mode of htg. (38) but which on fusion ring-closes with loss of aq. to 5-carbethoxy-2-mercapto-4-methylthiazole [Beil. XXVII-339], ndls. from alc., m.p. 150° (38), 141° (39).]

[C̄ with urea in alc. contg. a little aq. HCl gives on stdg. 5 months (36) 5-carbethoxy-2-hydroxy-4-methylimidazole [Beil. XXV-216], ndls. from aq. or tbls. from alc., m.p. 218° (36). — C̄ (1 mole) with thiourea (1 mole) at 90° reacts vigorously eliminating H_2O and giving (alm. quant. yield (37)) as the hydrochloride 2-amino-5-carbethoxy-4-methylthiazole [Beil. XXVII-338]; addn. of alk. sets free the base, ndls. from ether/alc., m.p. 175° (37) (13).]

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[illegible] –364 (1936). (12) von Meyer, von Findeisen, *J.* [illegible] rend, Schreiber, *Ann.* **318**, 381 (1901). (14) [illegible] *Gazz. chim. ital.* **22**, II 40–41 (1892). (16) [illegible] sagne, *Bull. soc. chim.* (4) **1**, 914–916 (1907).

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3:6208 DICHLOROACETIC ACID

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 Cl
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HC—COOH
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 Cl
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$C_2H_2O_2Cl_2$ Beil. II - 202, II_1-(90), II_2-(194)

B.P.		M.P.			
195°	(1) (62)	**13.25°**	(17)	D_4^{25} = **1.5579** (28)	
194.5–195°	(2)	**13.00°**	(18)		
194.42° at 760 mm.	(3)	**12.15°**	(17)	D_{25}^{25} = **1.5604** (4)	
194.0–194.5° cor.	(4)	**11°**	(19) (20)		
194°	(5) (6)	**10.85°**	(21)	D_{22}^{22} = **1.5594** (14)	n_D^{22} = **1.4659** (8)
193.5–193.9°	(7)	*10.8°*	(22)		
192.5° at 763 mm.	(28)	**10°**	(23) (28)	D_4^{20} = **1.5648** (28); **1.5642** (27)	n_D^{20} = **1.46582** (27)
192–193° cor., dec.	(8)	**9.7°**	(24) (25)	**1.5634** (8)	
191° at 760 mm.	(9)	**5–6°**	(14)		
190°	(10)	**−4.1°**	(24)	D_{20}^{20} = **1.5666** (8)	
189–191°	(11)	**−4°**	(26)		
		See Note 2.		D_4^{19} = **1.5691** (29)	n_D^{19} = **1.4667** (29)
				D_4^{15} = **1.5717** (28)	
				D_{15}^{15} = **1.5707** (27)	
144° at 164 mm.	(12)			See Note 3.	See Note 3.
140° at 142 mm.	(12)				
129° at 88 mm.	(12)				
125° at 71 mm.	(12)				
111.5° at 36 mm.	(12)				
105° at 25 mm.	(13)				
102.5° at 24 mm.	(12)				
99° at 21 mm.	(12)				
102°cor. at 20 mm.	(8) (14)				
102°u.c. at 20 mm.	(16)				
95–96° at 17 mm.	(8)				
91–92° at 12 mm.	(15)				
See Note 1.					

Note 1. The b.p. of C̄ at normal press. is not very significant, some decompn. to dichloroacetyl chloride (3:5290), phosgene (3:5000), and tarry products always occurring (8).

Note 2. C̄ apparently can exist in at least two crystn. modifications (24); no clear-cut study of the matter, however, has been reported.

Note 3. For values of D_{20}^{20} and n_D^{20} for aq. solns. of C̄ see (27).

[*See also chloroacetic acid* (3:1370) *and trichloroacetic acid* (3:1150).]

C̄ when pure is a colorless liq. which does not fume in moist air and which dissolves in

aq. without opalescence. — Ordinary comml. samples of C̄ may contain also chloroacetic acid (3:1370) and trichloroacetic acid (3:1150) as well as decompn. products from these or from C̄ itself, cf. (30) (31).

MISCELLANEOUS PHYSICAL PROPERTIES OF C̄

Adsorption of C̄. [For studies of adsorption of C̄ by activated carbon, charcoal, etc., see (32) (33) (34) (35) (36) (39); by silica gel see (33); by cellulose (viscose) see (37); by hide powder see (38).]

Distribution of C̄ between solvents. [For studies and data on distribution of C̄ between *aq. + ether* at 25° (40) (41); *aq. +* C_6H_6 at 15° (42) (43) (44) (45); *aq. + nitrobenzene* (43); *aq. + toluene* (43); *aq. + o-nitrotoluene* (43) (47); *aq. +* $CHCl_3$ (3:5050) (43); *aq. +* CCl_4 (3:5100) (43) (46); *aq. + EtBr* (43) (46); *aq. (contg.* $MgSO_4$*) + di-n-butyl ether* (1:7950) (48); *aq. + olive oil* (49); *acetone + glycerol* (50) see indic. refs.]

Binary systems contg. C̄. [For f.p./compn. data on systems *C̄ + trichloroacetic acid* (3:1150) (25); *C̄ + AcOH* (1:1010) (25); *C̄ + crotonic acid* (1:0425) (25); *C̄ + benzoic acid* (1:0715) (25); *C̄ + o-toluic acid* (1:0690) (25); *C̄ + m-toluic acid* (1:0705) (25); *C̄ + p-toluic acid* (1:0795) (25); *C̄ + phenylacetic acid* (1:0665) (25); *C̄ + cinnamic acid* (1:0735) (25); *C̄ + 2,6-dimethylpyrone* (24); *C̄ + azobenzene* (19); *C̄ + urea* (51); *C̄ + ethyl carbamate (urethane)* (51) see indic. refs.]

PHYSIOLOGICAL BEHAVIOR OF C̄

[For study of toxicity of C̄ see (52); for action of C̄ on human skin see (53) (54).]

PREPARATION OF C̄

From Various Chloro Compounds

From chloral hydrate. [For prepn. of C̄ from chloral hydrate (3:1270) with aq. NaCN + $CaCO_3$ (yields: 88–92% (55), 90% (15)) or with aq. NaCN (60–65% yield (16)) or with $K_3Fe(CN)_6$ (63) see indic. refs.; cf. also (56) (57); note here also the closely related matter of conversion of anhydrous chloral (3:5210) with alcohols + KCN (58) to the corresponding alkyl dichloroacetates, e.g., with MeOH to methyl dichloroacetate (3:5655) or with EtOH to ethyl dichloroacetate (3:5850), etc.; also conversion of chloral hydrate (3:1270) in ether with KCN + conc. aq. NH_4OH to (65–78% yield (59)) cf. (58) α,α-dichloroacetamide (see also below).]

From trichloroacetic acid. [For prepn. of C̄ from trichloroacetic acid (3:1150) by partial reduction with Zn + aq. (13), with Cu powder in aq. (80% yield (14)) or C_6H_6 + aniline (75–85% yield (8)) cf. (60), or by electrolytic reduction (80% yield (61)) see indic. refs.]

From chloroacetic acid. [For prepn. of C̄ from chloroacetic acid (3:1370) with Cl_2 (1), or Cl_2 in pres. of I_2 (62), see indic. refs.]

From dichloroacetaldehyde. [For prepn. of C̄ from dichloroacetaldehyde (3:5180) by oxidn. with HNO_3 see (2).]

From other misc. chloro compounds. [For formn. of C̄ from ethyl dichloroacetate (3:5850) with HCl gas (100% yield (11)); from dichloroacetyl chloride (3:5290) by hydrolysis or by disproportionation with AcOH (acetyl chloride (3:7065) also being formed (64)); from β,β,β-trichloro-α-hydroxypropionic acid (trichlorolactic acid) [Beil. III-286, III_1-(111), III_2-(210)] or its ethyl ester with excess aq. $Ba(OH)_2$ (65); from β,β-dichloro-α-acetoxyacrylonitrile [Beil. III_1-(135), III_2-(254)] with boilg. aq. (66) or from α,β,β-trichloro-α-acetoxypropionitrile [Beil. III-288, III_1-(112)] with 33% H_2SO_4 (66); from 2,2,4,4,6,6-hexachlorocyclohexantrione-1,3,5 (hexachlorophloroglucinol) [Beil. VII-854,

VII_1-(469)] with aq. (*sym.*-tetrachloroacetone (3:6050) is also formed) (67); from *unsym.*-dichloroacetone (3:5430) by oxidn. with HNO_3 + air (68); from 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with air in ultra-violet light in pres. of water (21) cf. (69); from pentachloroethane (3:5880) by partial hydrolysis with 88–97% H_2SO_4 at 168° (90% yield (70)) see indic. refs.]

From miscellaneous non-chlorinated compounds. [For formn. of $\bar{C}$ from AcOH with Cl_2 (71) in presence of I_2 (62) see indic. refs.; from acetylene with HOCl at 75–80° see (72); from ethyl acetoacetate (1:1710) with aq. bleaching powder (yield 60%) see (73); from phloroglucinol (1:1620) with aq. Cl_2 see (74) (75); from pyrrole with NaOCl see (76).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Behavior as an Acid

Acid strength of $\bar{C}$. $\bar{C}$ in aq. soln. is a strong acid [ionization const. at 25° is $K = 5.14 \times 10^{-2}$ (77) cf. (78) (18), at 18° $K = 5.15 \times 10^{-2}$ (45); for studies of activity coefficient of $\bar{C}$ in aq. and in salt solns. see (18) (48). — For tests on corrosion of metals by $\bar{C}$ see (16)].

[Studies of acid strength of $\bar{C}$ in other solvents include the following: in aq. MeOH (79) (81), in aq. EtOH (79) (80), in abs. EtOH (82), in *n*-BuOH (5) (83), in C_6H_6 (84), in chlorobenzene (85), in formamide (86), in acetonitrile (87).]

$\bar{C}$ on titration gives Neut. Eq. = 129.

Salts of $\bar{C}$. This topic cannot be exhaustively treated here but following examples are cited.

Salts with inorganic bases. [$NH_4\bar{A}$ (88); hydroxylamine salt, $HONH_3\bar{A}$, cryst. from C_6H_6/EtOH, m.p. 116.0–116.5° (89); $Na\bar{A}$ (on electrolysis gives (90) H_2, CO_2, CO, and also (91) dichloromethyl dichloroacetate, $K\bar{A}$, lfts. from alc. (11), on dry distn. gives (92) $\bar{C}$ + KCl + CO_2 + carbon, $Ca\bar{A}_2$, ndls. from abs. alc. (93); $Ca\bar{A}_2.3H_2O$ (93); $Cu\bar{A}_2$ (88); $Cu\bar{A}_2.4H_2O$ (88); $Cd\bar{A}_2.H_2O$ (94); $Mn\bar{A}_2.1\frac{1}{2}H_2O$ (94); $Co\bar{A}_2.3H_2O$ (94); note that all the foregoing salts are sol. aq.]

[Inorg. salts of $\bar{C}$ which are sparingly sol. aq. include the following: $Ag\bar{A}$ (93); $Th(OH)_2\bar{A}_2$ (96); $(UO)\bar{A}_2.2H_2O$ (97).]

Salts with organic bases (amines). [*Aniline dichloroacetate*, m.p. 122–123° (8) (98) cf. (30) (159) (note that this prod. or its components at 140° for 24 hrs. gives (98) dichloroacetanilide, m.p. 118°). — *o-Toluidine dichloroacetate*, m.p. 132.5° (98), 140° (99) (note that this prod. or its components at 140° for 18 hrs. gives (98) dichloroaceto-*o*-toluidide, m.p. 133°, but depressing m.p. of the salt to as low as 112°). — *p-Toluidine dichloroacetate*, m.p. 138° (98) (note that this prod. or its components on htg. gives (98) dichloroaceto-*p*-toluidide, m.p. 154°). — *Piperazine bis-(dichloroacetate)*, m.p. 181° cor. (100). — *Semicarbazide dichloroacetate*, m.p. 108° (101). — For salts of $\bar{C}$ with other org. amines see (30) (99).]

Esterification of $\bar{C}$. [For this see the text of methyl dichloroacetate (3:5655), ethyl dichloroacetate (3:5850), *n*-propyl dichloroacetate (3:6000), isopropyl dichloroacetate (3:5890); for study of direct esterification of $\bar{C}$ with various butyl and amyl alcs. without cat. see (102).]

Conversion of $\bar{C}$ to corresp. acid chloride. $\bar{C}$ with PCl_3 (103), with HCl gas + P_2O_5 (104), with $SOCl_2$ (poor yield apparently due to much formn. of dichloroacetic acid anhydride (3:6430) (105) (106) (107) (108)), with BzCl (3:6240) (73% yield (111)), or with benzotrichloride (3:6540) (109) (110) gives dichloroacetyl chloride (3:5290), b.p. 108°.

Addition reactions of $\bar{C}$ with org. cpds. $\bar{C}$ in pres. of suitable cat. adds to olefins yielding corresp. esters [e.g., $\bar{C}$ with propylene + BF_3 as directed gives (39.5% yield (112)) isopropyl dichloroacetate (3:5890); $\bar{C}$ with 2-methylbutene-2 (trimethylethylene) (1:8220) at 18°

shows slight tendency toward formn. of corresp. ester in C_6H_6, $CHCl_3$ or CS_2 but none in alc. or ether (113)].

[$\bar{C}$ with ethylene oxide (1:6105) in dry ether at 0° gives (15% yield (114)) cf. (115) β-hydroxythyl dichloroacetate (3:9107).]

Behavior of $\bar{C}$ as Dichloro Compound

Reduction. [$\bar{C}$ in alc. KOH soln. with H_2 + $Pd/CaCO_3$ splits off all its halogen as HCl (116). — $\bar{C}$ with Zn + water on htg. is slowly reduced to chloroacetic acid (3:1370) but reaction is much less energetic than that of trichloroacetic acid (3:1150) under same conditions (13).]

Hydrolysis of halogen atoms of $\bar{C}$ or its salts. [$\bar{C}$ with aq. in s.t. at 100° is slowly or in pres. of NaOH or $Ba(OH)_2$ rapidly decomposed (93) cf. (117). — For study of kinetics of hydrolysis of $\bar{C}$ see (118) (119). — Note, however, that $Ag\bar{A}$ on htg. with aq. (93), or $\bar{C}$ (or its salts) on hydrolysis at elevated temp. and press. (120), or salts of $\bar{C}$ htd. with aq. solns. of NaOAc or NaOBz (121), gives glyoxylic acid, OHC–COOH [Beil. III-594, III_1-207, III_2-(385)], m.p. 98°, very sol. aq. — For a method of detn. of $\bar{C}$ in pres. of chloroacetic acid (3:1370) and trichloroacetic acid (3:1150) based on this hydrolysis see (122).]

Behavior of $\bar{C}$ with alkoxides. [$\bar{C}$ (as $K\bar{A}$) with excess MeOH/NaOMe refluxed under H_2, and the solution then further esterified with MeOH/HCl, gives (62% yield (123)) cf. (124) methyl dimethoxyacetate, b.p. 60–61° at 12 mm., $D_4^{18} = 1.0962$, $n_D^{18} = 1.4045$ (124); this ester upon alk. hydrolysis gives (85.7% yield (124)) dimethyoxyacetic acid (glyoxylic acid dimethylacetal) as a sirup.]

[$\bar{C}$ with excess EtOH/NaOEt under reflux followed by acidification and esterification as above gives (50% yield (125)) (126) ethyl diethoxyacetate [Beil. III-601, III_1-(210), III_2-(389)], b.p. *199° (127), 94–98° at 19 mm. (125), 83–85° at 13 mm. (125).]*

[$\bar{C}$ in excess EtOH/NaOEt with Na phenolate refluxed 14 hrs., then acidified and esterified as above, gives (61% yield (128)) ethyl diphenoxyacetate [Beil. VI-170], oil, b.p. 240° at 53 mm. (129), 166–168° at 0.8 mm. (128). — However, $\bar{C}$ with phenol in aq. NaOH on htg. and acidification gives (130) (131) diphenoxyacetic acid, ndls. from pet. ether or aq. AcOH, m.p. 91° (129) (130).]

Condensation with hydrocarbons. $\bar{C}$ with aromatic hydrocarbons on htg. condenses with elimination of 2 HCl giving diarylacetic acids [e.g., $\bar{C}$ with naphthalene at 180° for 60–100 hrs. gives (132) di-(α-naphthyl)acetic acid [Beil. IX-720, IX_1-(313)], cryst. from CCl_4, m.p. 224° (133), 223° u c. (134); for analogous behavior of $\bar{C}$ with other hydrocarbons see (132)].

Behavior of $\bar{C}$ with RMgX compounds. [$\bar{C}$ with C_6H_5MgBr (large excess) in ether soln. followed by usual hydrolysis gives (34% yield (135)) α,α,β-triphenylethylene glycol, ndls. from C_6H_6, m.p. 163° (135).]

Behavior of $\bar{C}$ with hydroxylamine. [$\bar{C}$ (1 mole) with $NH_2OH.HCl$ (1 mole) + aq. KOH (4 moles) at 60° for 4 hrs. gives (136) isonitrosoacetic acid (glyoxylic acid oxime) [Beil. III-599, III_1-(208), III_2-(389)], cryst. from dry ether, m.p. 138° (136) (note that this prod. forms with water a monohydrate, m.p. about 70° (137)).]

Behavior of $\bar{C}$ with aromatic amines. (See also salt formation above.)

With aniline. The products of reaction of $\bar{C}$ on htg. with aniline are disputed [on one hand $\bar{C}$ (1 mole) with aniline (4 moles) at 100°, then evapd. with NaOAc, is claimed (138) (139) to give 4,4′-diaminodiphenylacetic acid [Beil. XIV-540, XIV_1-(625)], m p. about 195° (140); on the other hand. the prod. is regarded by some (141) (142) as a mixt. of two stereoisomeric forms of 2,2′(?)-diaminostilbene-α,α'-dicarboxylic acids [Beil. XIV-573]].

With o-toluidine. [$\bar{C}$ (1 mole) with o-toluidine (4 moles) at 100° gives (140) (143) 4,4′-diamino-3,3′-dimethyldiphenylacetic acid [Beil. XIV-543, XIV_1-(627)], ndls. from alc.,

m.p. 239–240° (143) dec. (140), accompanied by some 7-methylisatin-3-(*o*-tolylimide) [Beil. XXI-512], yel. lfts. from alc., m.p. about 225° dec. (138).]

With p-toluidine. [Č (1 mole) with *p*-toluidine (4 moles) at 100° in aq. or alc. soln. gives (144) (145) 5-methylisatin-3-(*p*-tolylimide) [Beil. XXI-510, XXI_1-(401)], golden-yel. ndls. or lfts. from alc., m.p. 259° (144) (145).]

Behavior of Č with urea. Č with urea (2 moles) in pres. of NaOEt condenses to give (146) 5-ureidohydantoin (allantoin) [Beil. XXV-474, XXV_1-(692)], m.p. by ord. htg. in cap. tube is 228–230° (147), by rap. htg. in bath already at 228° is 233–234° (147).

Behavior of Č with arylhydrazines. Č with arylhydrazines in alc. KOH yields a mixt. of the two stereoisomeric arylhydrazones of glyoxylic acid [e.g., Č with phenylhydrazine in dil. alc. KOH refluxed 2 hrs. gives (148) a mixt. of the α-glyoxylic acid phenylhydrazone, m.p. abt. 138° with decompn. at 142–143°, and the β-glyoxylic acid phenylhydrazone, m.p. 128–129° dec. (rap. htg.) (148); for analogous behavior of Č with other arylhydrazines see (148)].

Ⓟ **Color test with NH_4OH/Cu_2Cl_2 reagent.** Č on shaking in filled stoppered bottle with conc. aq. NH_4OH contg. Cu_2Cl_2 gives dark blue color within 3 min. (149); note, however, that the same behavior is shown by trichloroacetic acid (3:1150).

—— **Methyl dichloroacetate:** oil, b.p. 143° (see 3:5655).

—— **Ethyl dichloroacetate:** oil, b.p. 158° (see 3:5850).

—— **Benzyl dichloroacetate:** oil, b.p. 179° at 60 mm. (150). [From Č with benzyl alcohol (1:6480) with HCl gas (150).]

—— **Phenyl dichloroacetate** [Beil. VI-153, VI_1-(87)]: m.p. 48° (151), b.p. 247.5° cor. (151). [From dichloroacetyl chloride (3:5290) + $AlCl_3$ in CS_2 (prod. m.p. 33° was probably impure (152)).]

—— ***p*-Tolyl dichloroacetate:** m.p. 58° (151). [Prepd. indirectly from α,β-dichlorovinyl ethyl ether (3:5440) with *p*-cresol (1:1410) (151).]

—— ***p*-Nitrobenzyl dichloroacetate:** oil, unsuitable as Ⓓ (160) (161).

—— **Phenacyl dichloroacetate:** oil (153).

—— ***p*-Chlorophenacyl dichloroacetate:** m.p. 93.0–93.8° (153).

—— ***p*-Bromophenacyl dichloroacetate:** m.p. 98.2–99.3° (153).

—— ***p*-Iodophenacyl dichloroacetate:** unreported.

—— ***p*-Phenylphenacyl dichloroacetate:** unreported.

Ⓓ ***S*-Benzylthiuronium dichloroacetate:** m.p. 178–179° (154). [Note that for corresp. salts from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) the values are respectively 159–160° and 148–149° (154).]

—— ***S*-(*p*-Chlorobenzyl)thiuronium dichloroacetate:** unreported.

—— ***S*-(*p*-Bromobenzyl)thiuronium dichloroacetate:** unreported.

—— **α,α-Dichloroacetamide:** cryst. from C_6H_6, m.p. 99.4° (155), 98.5–99° (58), 98.5° (156), 97.5–99.5° (59). [From ethyl dichloroacetate (3:5850) with aq. NH_4OH (155) or in other indirect ways, e.g., from chloralammonia with KCN + aq. NH_4OH (93% yield (58)), or from chloral hydrate (3:1270) with KCN + aq. NH_4OH (65–78% yield (59)).] — [Note that dichloroacetamide forms with bromo-chloro-acetamide or with chloro-iodo-acetamide an unbroken series of mixed crystals.]

Ⓓ **α,α-Dichloroacetanilide:** colorless ndls. from alc. or by sublimation, m.p. 118° (98), 117.7° (156). [From Č with aniline at 140° for 24 hrs. (98) or from dichloroacetyl chloride (3:5290) with aniline in C_6H_6 (157) or acetone (157).] — [Note that this prod. forms with α-bromo-α-chloroacetanilide, m.p. 116.8° (157), a series of mixed cryst. and with α-chloro-α-iodoacetanilide, m.p. 142.3°, a eutectic, m.p. 105.2° (157).] — [Note also that aniline dichloroacetate (see also above) has m.p. 122–123° (98).]

Ⓓ α,α-Dichloroacet-o-toluidide: cryst. from 50% alc. or by sublimation, m.p. 133° (98). [From C̄ + o-toluidine at 140° for 18 hrs. (98); note that the salt o-toluidine dichloroacetate has same m.p. 132.5° as the α,α-dichloroacet-o-toluidide but that the m.p. of a mixture of the two compds. is depressed to below 112° (98).]

—— α,α-Dichloroacet-p-toluidide: pl. from alc. or by sublimation, m.p. 154° (98). [From C̄ + p-toluidine at 148° for 18 hrs. (98); note that the corresp. salt, p-toluidine dichloroacetate, has m.p. 138° (98).]

—— α,α-Dichloroacet-N-benzylamide: m.p. 96.2° (156), 94.8–95.6° cor. (158), 94.2–95.0° u.c. (158). [From ethyl dichloroacetate (3:5850) (158) cf. (162) or dichloroacetyl chloride (3:5290) (156) with benzylamine; note, however, that the corresp. derivs. from chloroacetic acid (3:1370) and from trichloroacetic acid (3:1150) have almost the same m.p.'s, viz., 93.0–93.6° cor. and 93.6–94.4° cor., respectively (158).]

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Ber. **18**, 190–193 (1885). [illegible] U.S. 2,158,098, May 16, 1939; *Cent.* **1939**, II 435[illegible], Moffett, Dickey, *Org. Syntheses*, Coll. Vol. 2 (1[illegible]ch, Achterfeldt, Seufert, *J. prakt. Chem.* **92**, 1–40 [illegible] **41**, 1130 (1919). (150) Seubert, *Ber.* **21**, 283 (1888).
(151) Crompton, Triffitt, *J. Chem. Soc.* **119**, 1875 (1921). (152) Kunckell, Johannsen, *Ber.* **31**, 171 (1898). (153) Lundqvist, *J. Am. Chem. Soc.* **60**, 2000 (1938). (154) Veibel, Ottung, *Bull. soc. chim.* (5) **6**, 1435 (1939). (155) Taylor, Forscey, *J. Chem. Soc.* **1930**, 2276. (156) McKie, *J. Chem. Soc.* **123**, 2214–2217 (1923); **125**, 1076–1079 (1924). (157) Votocek, Burda, *Ber.* **48**, 1005–1006 (1915). (158) Buehler, Mackenzie, *J. Am. Chem. Soc.* **59**, 421–422 (1937). (159) Beamer, Clarke, *Ber.* **12**, 1067 (1879). (160) Lyons, Reid, *J. Am. Chem. Soc.* **39**, 1742 (1917).
(161) Lundqvist, *J. Am. Chem. Soc.* **60**, 2000 (1938). (162) Dermer, King, *J. Org. Chem.* **8**, 168–173 (1943).

—— TRICHLOROACETIC ACID $Cl_3C.COOH$ $C_2HO_2Cl_3$ **Beil. II - 206**
II_1-(92)
II_2-(196)

B.P. 196° **M.P. 57°**

See 3:1150. *Division A: Solids.*

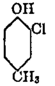
3:6210 ACETALDEHYDE *bis*-(β-CHLOROETHYL)ACETAL $C_6H_{12}O_2Cl_2$ **Beil. S.N. 79**
$CH_3.CH(O.CH_2.CH_2Cl)_2$
(α,α-*bis*-(β-Chloroethoxy)ethane)

B.P. 194–196° dec. (2) D_{19}^{19} = **1.1712** (2) $n_D^{19.2}$ = **1.4532** (2)
109–110° at 30 mm. (1)
106–108° at 17 mm. (2)
106–107° at 14 mm. (3)

Colorless liq. with odor resembling dichloroacetaldehyde diethylacetal (3:6110).
[For prepn. of C̄ from ethylene chlorohydrin (3:5552) with acetaldehyde (1:0100) + dry HCl (36% yield (2)) see (2) (1); with acetylene + BF_3 (71% yield) see (3).]

3:6210 (1) Street, Adkins, *J. Am. Chem. Soc.* **50**, 162–167 (1928). (2) Grignard, Purdy, *Bull. soc. chim.* (4) **31**, 985–986 (1922). (3) Nieuwland, Vogt, Foohey, *J. Am. Chem. Soc.* **52**, 1018–1024 (1930).

3:6215 2-CHLORO-4-METHYLPHENOL C_7H_7OCl **Beil. VI - 402**
(2-Chloro-*p*-cresol) **VI_1—**
VI_2-(383)



B.P. 195–196° at 760 mm. (2) D_4^{27} = **1.1785** (10) n_D^{27} = **1.5200** (10)
197–198° at 738 mm. D_{25}^{25} = **1.2106** (1)
195–197° (10)

Clear odorless liq. with characteristic disagreeable persistent odor. — Slightly sol. aq.; sol. alc., ether, C_6H_6.
[For prepn. from 2-chloro-4-methylaniline via diazo reaction see (3); from sodium *p*-cresolate in CS_2 see (1); from *p*-cresol with Cl_2 in CCl_4 (4) or with SO_2Cl_2 (77% yield (10)) see indic. refs.]
C̄ in 5 pts. AcOH and treated with 2 pts. conc. HNO_3 (D = 1.4), or C̄ dislvd. in 10 pts.

AcOH and grad. treated with powd. $NaNO_2$ (5), yields on pptn. with aq. 2-chloro-4-methyl-6-nitrophenol [Beil. VI-413], golden-yel. ndls. from dil. alc. or dil. AcOH, m.p. 65° (5). [Note that addition of C̄ to fumg. HNO_3 ($D = 1.5$) leads to its oxidn. (evoln. of nitrous fumes), nitration, and wandering of methyl group (6).]

The methyl ether of C̄ [Beil. VI-403], 2-chloro-4-methylanisole, b.p. 215–218° cor. at 760 mm., has been prepd. only indirectly.

Ⓓ 2-Chloro-4-methylphenyl benzoate: pl. from pet. eth., m.p. 71–72° (7). [This benzoate htd. with 0.7 of its wt. of $AlCl_3$ for 10 min. at 140° gives by Fries rearrangement 92% yield (8) of 2-hydroxy-3-chloro-5-methylbenzophenone, yel. lfts. from MeOH, m.p. 71° (8) cf. (9).]

3:6215 (1) Schall, Dralle, *Ber* **17**, 2528–2529 (1884). (2) Klarmann, Shternov, Gates, *J. Am. Chem. Soc.* **55**, 2585 (1933) (3) Cain, Norman, *J Chem Soc.* **89**, 24 (1906). (4) Zincke, *Ann.* **328**, 277 (1903). (5) Zincke, *Ann.* **328**, 311–312 (1903). (6) Zincke, *Ann.* **328**, 314 (1903). (7) von Auwers, *Ber* **44**, 801 (1911). (8) Rosenmund, Schnurr, *Ann* **460**, 86 (1928). (9) von Auwers, Mauss, *Ann.* **464**, 310 (1928). (10) Sah, Anderson, *J. Am. Chem. Soc.* **63**, 3165 (1941).

3:6220 β,γ-DICHLORO-*n*-PROPYL ACETATE $C_5H_8O_2Cl_2$ Beil. II - 129

(Glycerol α,β-dichlorohydrin α-acetate, γ-aceto-α,β-dichlorohydrin)

CH_2Cl
|
$HC—Cl$
|
$CH_2.O.CO.CH_3$

Beil. II - 129, II_1-(58), II_2—

B.P. 197–198°	(1)	$D_{15}^{15} = 1.1672$ (3)
191–192° cor. at 755 mm.	(2)	
115–120° at 40 mm.	(3) (4)	
89–91° at 16 mm.	(5)	
81–83° at 12 mm.	(2)	

[For prepn. of C̄ from 2,3-dichloropropanol-1 ("β-dichlorohydrin") (3:6060) with Ac_2O see (3); from glycerol α,α′-diacetate with PCl_5 or S_2Cl_2 see (2); from allyl chloride (3:7035) with acetyl hypochlorite see (6).]

C̄ on keeping decomposes, perhaps by hydrolysis (2). [For study of hydrolysis with N/10 HCl see (1).] — C̄ with MeOH + trace HCl gives by alcoholysis (5) (6) 2,3-dichloropropanol-1 (3:6060) + MeOAc

3:6220 (1) Bancroft, *J Am Chem. Soc.* **41**, 425 (1919). (2) Wegscheider, Zmerzlikar, *Monatsh.* **34**, 1074–1079 (1913). (3) de la Acena, *Compt rend* **139**, 868 (1904). (4) Gibson, *J. Soc. Chem. Ind* **50**, 950 (1931). (5) Delaby, Dubois, *Bull. soc. chim.* (4) **47**, 572 (1930). (6) Bockemüller, Hoffmann, *Ann.* **519**, 189–190 (1935).

3:6230 β-CHLOROETHYL CHLOROACETATE $C_4H_6O_2Cl_2$ Beil. II - 198

$ClCH_2CH_2\ O.CO.CH_2Cl$

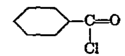
II_1—
II_2—

B.P. 197–198°	(1)	D[illegible] = 1.317 (1)
91–95° at 12 mm.	(3)	

[For prepn. from ethylene chlorohydrin (3:5552) + chloroacetyl chloride (3:5235) see (1); for prepn. from ethylene oxide (1:6105) + chloroacetyl chloride see (3).]

C̄ on boiling with aq. hydrolyzes to β-chloroethanol (3:5552) and chloroacetic ac. (3:1370).

3:6230 (1) Henry, *Bull. soc. chim* (2) **42**, 260 (1884). (2) Mulder, Bremer, *Ber.*, **11**, 1960 (1878). (3) Altwegg, Landrivon, U.S 1,393,161, Oct. 11, 1921; *Cent.* **1922**, IV 947.

3:6240 BENZOYL CHLORIDE  C_7H_5OCl Beil. IX - 182
IX_1-(94)

B.P.			M.P.		
199°	at 760 mm.	(1) (25)	−0.5° (4) (22)	D_4^{25} = 1.2070 (20)	n_D^{25} = 1.5520 (9)
198.3°	at 749.4 mm.	(1)	−0.6° (3)		1.5508 (20)
198–198.3 cor.	at 749.4 mm.	(2)	−1.0° (1) (23)	$D_4^{20.9}$ = 1.2105 (24)	$n_D^{20.9}$ = 1.55376 (24)
197.9°		(3)			
197.3°	at 754 mm.	(4)		D_4^{20} = 1.2122 (14)	
197.21°	at 760 mm.	(5)		1.2113 (4)	
197.2°–197.3°		(6)			n_D^{20} = 1.55369 (14)
197.2° cor.	at 760 mm.	(7)			1.55354 (3)
197.1–197.6°		(8)			1.5536 (4)
197°		(9)		D_4^{15} = 1.2188 (25)	
196.8–197.0°	at 764 mm.	(10)			n_D^{15} = 1.55799 (25)
196.2–196.5° cor.	at 761.3 mm.	(11)			
196.8° cor.	at 745 mm.	(12)			
194.5–196° cor.	at 746 mm.	(13)			
193.9–194.1°	at 742.2 mm.	(14)			

100.5°	at 35.5 mm.	(10)	83.47°	at 16 mm.	(5)	75°	at 10.5 mm.	(10)
96.1°	at 30 mm.	(10)	82.5°	at 15.5 mm.	(10)	74°	at 10 mm.	(10)
94.5°	at 29 mm.	(10)	82.10°	at 15 mm.	(5)	74.0–74.2°	at 9.5 mm.	(8)
92.5°	at 25 mm.	(10)	80.59°	at 14 mm.	(5)	71°	at 9 mm.	(10)
93°	at 20 mm.	(15)	79°	at 13 mm.	(10)	77.8–78.0°	at 8 mm.	(18)
87.5°	at 20 mm.	(10)	82°	at 12 mm.	(16)	67.6–67.8°	at 7.5 mm.	(19)
87°	at 19.5 mm.	(10)	78.8°	at 10.5 mm.	(17)	49–50°	at 2.5–3.0 mm.	(20)

Note 1. For vapor press. of $\bar{C}$ for range T = 85.4–105.5° see also (21).

MISCELLANEOUS PHYSICAL PROPERTIES OF $\bar{C}$

BINARY SYSTEMS CONTAINING $\bar{C}$

$\bar{C}$ + inorganic compounds. *$\bar{C}$ + $AlCl_3$:* m.p. 93° (22), 95° (26); for prepn. from $\bar{C}$ + $AlCl_3$ in CS_2 see (26); for thermal anal. (eutectic with $\bar{C}$ has m.p. −7.5° and conts. 87.3 wt. % $\bar{C}$) see (22); for conductivity of $AlCl_3$ in $\bar{C}$ see (27); for study of mol. wt. in C_6H_6 see (28).

$\bar{C}$ + $AlBr_3$: m.p. 90° (22); for thermal anal. (eutectic with $\bar{C}$ has m.p. −5° and conts. 77.8 wt. % $\bar{C}$ while eutectic with $AlBr_3$ has m.p. abt. 7–8° and conts. 21 wt. % $\bar{C}$) see (22); see also (30)

—*$\bar{C}$ + $FeCl_3$:* scarlet red hygroscopic ndls. (31); for conductivity see (28).

$\bar{C}$ + $SbCl_3$: for thermal anal. (eutectic with $\bar{C}$ has m p. −23° and conts. 55 wt. % $\bar{C}$) see (32).

$\bar{C}$ + $SbCl_5$: for prepn. see (34); for conductivity in liq. SO_2 see (33).

$\bar{C}$ + $SbBr_3$: for thermal anal. (eutectic with $\bar{C}$ has m.p. −6° and conts. 68 wt. % $\bar{C}$) see (32).

$\bar{C}$ + organic compounds. *$\bar{C}$ + C_6H_6:* for thermal anal. (eutectic has m.p. −26.8° and conts. 63 6 wt. % $\bar{C}$) see (35). — *$\bar{C}$ + p-xylene:* for thermal anal. (eutectic has m.p. −18 5° and conts. 67.2 wt. % $\bar{C}$) see (35). — *$\bar{C}$ + mesitylene:* for thermal anal. (eutectic has m.p. abt. −70° and conts. abt. 20 wt. % $\bar{C}$) see (35). — *$\bar{C}$ + biphenyl:* for thermal anal. (eutectic has m.p. −8° and conts 81 8 wt. % $\bar{C}$) see (35). — *$\bar{C}$ + diphenylmethane:* for thermal anal. (eutectic has m.p. −15° and conts 66.7 wt. % $\bar{C}$) see (35).

$\bar{C}$ + chlorobenzene: for thermal anal. (eutectic has m.p. −54.2° and conts. 19.3 wt. % $\bar{C}$) see (35) — *$\bar{C}$ + nitrobenzene:* for thermal anal. (eutectic has m.p. −20.5° and conts. 50 wt. % $\bar{C}$) see (35).

PREPARATION OF $\bar{C}$

Note that comml. $\bar{C}$ is often contaminated with various chlorobenzoyl chlorides (e.g., *o*-chlorobenzoyl chloride (3.6640), *m*-chlorobenzoyl chloride (3:6590), *p*-chlorobenzoyl chloride (3:6550), etc.), with traces of benzaldehyde (1:0195), or with benzoic acid (1:0715) + HCl from hydrolysis. For removal of BzOH + HCl from $\bar{C}$ by shaking its C_6H_6 soln. with cold aq. 5% $NaHCO_3$ see (12); by treatment with metallic oxides or carbonates see (36).

From benzoic acid. [For prepn. of $\bar{C}$ from benzoic acid (1:0715) with PCl_5 (70% yield (37)) (10) (38), with PCl_3 (39) (40) in pres. of $ZnCl_2$ (77% yield (37)) or in pres. of a little aq. at 100° under press (41), with $SOCl_2$ (90% yield (37)) (42), with SCl_2 in CS_2 (43), with $SiCl_4$ directly (23% yield (44)) or in C_6H_6 (77% yield (44)), with $POCl_3$ + alkali chloride at elev. temp. (45), or with dry HCl + P_2O_5 at 200° (46) see indic. refs.]

[For prepn. of $\bar{C}$ from benzoic acid (1:0715) with NaCl + Na or K pyrosulfate at 200° (47), or with Na chlorosulfonate (48) cf. (49), see indic. refs.]

[For prepn. of $\bar{C}$ from benzoic acid (1:0715) with other organic acyl chlorides such as carbonyl chloride (phosgene) (3:5000) at 140–200° (50) or in pres. of tertiary bases (such as pyridine) or their salts (51), with oxalyl (di)chloride (3:5060) (98% yield (15)), with *p*-toluenesulfonyl chloride in pyridine (52), or with α,β-dichloroethyl ethyl ether (3:5640) (53). see indic refs.]

From salts of benzoic acid. Note that with salts of benzoic acid more or less formn. of benzoic anhydride (1:0595) may occur.

[For prepn of $\bar{C}$ from NaOBz with $POCl_3$ (2) (54), with SCl_2 at room temp. (55) cf. (43), with SO_2 + Cl_2 (56), with Na chlorosulfonate (48) cf. (49), or with benzenesulfonyl chloride (57) see indic. refs.]

[For prepn. of $\bar{C}$ from AgOBz with carbonyl chloride (3:5000) in s.t. at 100° see (58).]

From dibenzoyl peroxide. [For prepn. of $\bar{C}$ from dibenzoyl peroxide (1:4930) with oxalyl (di)chloride (3:5060) refluxed in dark for 24 hrs. (70% yield (59)), with PCl_5 in pet. ether (60), with $AlCl_3$ in $CHCl_3$ at 0° (61) or in C_6H_6 at 100° (62), or with $FeCl_3$ in C_6H_6 at 100° (62) see indic. refs.]

From other benzoic acid derivatives. [For formn. of $\bar{C}$ from benzamide with dry HCl or AcCl at 140° see (63); from methyl benzoate (1:3586) with PCl_5 at 160–180° (64) or from ethyl benzoate (1:3721) with PCl_5 in s t. at 140° (65) see indic. refs.; from α,β-dichloroethyl benzoate or from α-chloroethyl benzoate on htg. in pres. of traces of $ZnCl_2$ see (66); from benzoic anhydride (1:0595) with PCl_3 + Cl_2 (67) or with carbonyl chloride (3:5000) (68) see indic. refs.]

From benzaldehyde. [For formn. of $\bar{C}$ from benzaldehyde (1:0195) with SO_2Cl_2 (5 moles) on distn. (69), with S_2Cl_2 in s t. at 150° (107), with $POCl_3$ in C_6H_6 (70), with NOCl (71), with EtOCl (3:7022) (72), with *ter*-AmOCl (3:9287) (8.5% soln. in CCl_4) at room temp. for 15 hrs. (73), or with Cl_2 (91) (105) (106) see indic. refs.]

From benzotrichloride. [For prepn. of C̄ from benzotrichloride (3:6540) by partial hydrolysis with limited amt. of aq. in pres. of H_2SO_4 or $FeCl_3$ (74), with aq. vapor over tin phosphate at 240° (75), with ord. comml. $ZnCl_2$ at 120° (76) in pres. of limited aq. (77) (note that *pure* $ZnCl_2$ fails to react but addn. of 1 mole aq. or initial use of tech. $ZnCl_2$ gives C̄ (76)), with pure ZnO at 100° (76), with BzOH in boilg. nitrobenzene (78) or in pres. of $ZnCl_2$ (80), with NH_4OBz at 200–210° as directed (79), or with EtOH in pres. of $FeCl_3$ or Fe (81) see indic. refs.]

Note that benzotrichloride (3:6540) on heating with carboxylic acids or anhydrides, especially in pres. of $ZnCl_2$, is often employed to prepare a mixture of C̄ with the acid chloride corresponding to the acid or anhydride so employed, particularly in cases where the two acyl chlorides are readily separable. [E g., note that benzotrichloride (3:6540) with phthalic anhydride (1:0725) (81) (82) or phthalic acid (1:0820) (83) + $ZnCl_2$ at 110–120° gives (96% yield (82)) C̄ + (93% yield (82)) *sym.*-phthalyl (di)chloride (3:6900); benzotrichloride with AcOH (1:1010) in pres. of an acid cat. gives (84) (85) (86) (87) C̄ + acetyl chloride (3:7065); for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5420), fumaryl (di)chloride (3:5875), and terephthalyl (di)chloride (3:2205). Similarly, benzotrichloride (3:6540) with salts of sulfonic acids yields C̄ + the corresp. arylsulfonyl chlorides; e.g., benzotrichloride with sodium β-naphthalenesulfonate gives (88) 90% yield C̄ + 80% yield β-naphthalenesulfonyl chloride.]

From benzal (di)chloride. [For formn. of C̄ from benzal (di)chloride (3:6327) with O_2 in u.v. light (89), with air in pres. of Ni at 160° (90), or with BzOH (1:0715) + Cl_2 at 125–175° (91) see indic. refs.]

From miscellaneous sources. [For formn. of C̄ from benzyl alc. (1:6480) with Cl_2 (92) or with $SOCl_2$ at 180° (103), from benzyl acetate (1:3751) with Cl_2 at 150–170° (104), from thiobenzoyl chloride + O_2 at 100–120° (93), from benzonitrile with NOCl at 180° (94), from tolan (diphenylacetylene) with NOCl at 150–200° (95), from dibenzoyltartaric anhydride + PCl_5 (3 moles) in s t. at 130° for 3 hrs. (note that chlorofumaryl dichloride is also formed) (96), from *N,N*-dibenzoylaniline (dibenzanilide) with dry HCl at 250–270° (note that benzanilide is also formed) (97), from α-chloro-α-nitro-phenylacetamide on dry htg. (98), from phthalic anhydride (1:0725) + HCl gas + $CrCl_3$ or $ZnCl_2$ at 290–300° under press. (99), or from C_6H_6 (1:7400) with carbonyl chloride (phosgene) (3:5000) + $AlCl_3$ (100) (101), or with oxalyl (di)chloride (3:5060) + $AlCl_3$ (102) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Pyrolysis. [C̄ in N_2 through porcelain tube at 550–600° (108) or over Ni at 420° (109) cf. (110) gives CO, chlorobenzene (3:7903), and other products; C̄ over finely divided Cu at 420–450° gives (110) benzoic anhydride (1:0595) + HCl; C̄ over $BaCl_2$ at 420–450° gives (110) benzoic anhydride (1:0595) and other products. For study of effect of radium radiation at 2–12° over 7–8 month period see (13).]

Reduction. [C̄ with H_2 in boilg. xylene in pres. of PtO_2 + trace of thiourea (111), $Pd/BaSO_4$ (112), or powd. Ni (112), or C̄ over Pd at 200–230° (113) cf. (114) gives (yields: 96% (111), 87–89% (113)) benzaldehyde (1:0195); for study of purification of xylene as *solvent for cat. reduction of C̄ see (115); for study of influence of various other solvents* see (116) (112).]

[C̄ with H_2 in pres. of $NiCl_2$ at 270–280° gives (110) benzene, toluene, biphenyl + HCl; C̄ with copper hydride is claimed (117) to yield benzaldehyde but this could not be confirmed (118). C̄ with chromous acetate in 50% KOH gives (very small yield (119)), benzyl alc. (1:6480), while C̄ with LiH in high-boilg. pet. ether at 130° gives (presumably by subsequent condensation of the intermediate benzaldehyde) 65% yield (120) benzyl benzoate (1:4422).]

[$\bar{C}$ with Na/Hg + stream of dry HCl gives (121) benzyl alc. (1:6480); $\bar{C}$ with Na/Hg in dry ether gives (122) (123) (124) benzyl alc. (1:6480), benzoic acid (1:0715), benzil (1:9015), α,α'-dibenzoxystilbene ("isobenzil") [Beil. IX-138], and α,α'-dibenzoxydibenzyl [Beil. IX-136]; $\bar{C}$ with Na in moist ether gives (125) benzyl alc. (1:6480), benzoic acid (1:0715), and benzyl benzoate (1:4422).]

Oxidation. [$\bar{C}$ on oxidn. in pres. of hydrocarbon peroxides and various oxidn. cat. is claimed (126) to give dibenzoyl peroxide (1:4930); see also below under behavior of $\bar{C}$ with Na_2O_2.]

Chlorination. [$\bar{C}$ on monochlorination with Cl_2 at 35° in pres. of $FeCl_3$ gives (10) cf. (127) mainly a mixt. of chlorobenzoyl chlorides [83.5% *m*- (3:6590) + 14.5% *o*- (3:6640) + 2.0% *p*- (3:6550)] accompanied by a small amt. of dichlorobenzoyl chlorides; for extensive study of effect of using higher proportion of Cl_2 under otherwise same conditions see (128). Note, however, that $\bar{C}$ with 3 moles Cl_2 in s t. gives (129) (130) a mixt. of addn. products, such as 1,2,3,4,5,6-hexachlorohexahydrobenzoyl chloride, substitution products, and materials formed by both addition and substitution (130)]

Sulfonation. [$\bar{C}$ cannot be sulfonated without accompanying hydrolysis of the acyl chloride function (131) (132) (133) (134) (137), the end prod. of these sulfonation processes is, therefore, not *m*-sulfobenzoyl chloride (apparently still unknown cf. (135)) but rather *m*-sulfobenzoic acid [Beil. XI-384, XI_1-(98)]. However, $\bar{C}$ added to conc. H_2SO_4 at 0–40° gives (136) a cryst addn. prod. $\bar{C}.H_2SO_4$ which on stdg loses HCl forming benzoyl hydrogen sulfate [Beil. IX_1-(94)] but shows no transformation into *m*-sulfobenzoic acid even after 6 months over dry alkali even though HCl is lost completely (136). At 100° conversion of benzoyl hydrogen sulfate occurred very slowly and the prod. consisted of *o*-sulfobenzoic acid (not *meta*) (136).]

BEHAVIOR OF $\bar{C}$ WITH OTHER INORGANIC REAGENTS

$\bar{C}$ with HF. [$\bar{C}$ with HF as directed (138) (139) or with dry KHF_2 in Cu retort (140) (141) (142), with ZnF_2 at 195° (11) (143), with AgF in s.t. at 190° for 6 hrs. (144), or with 3 moles SbF_3 (145) gives (yields: 67–80% (140), 76% (145), 69% (11)) benzoyl fluoride, b.p. 161.5° at 745 mm. (142), 159° (139), 156° (146), 155–156° at 760 mm. (11), 155° (138), 154–155° (143), 151° u.c. at 736 mm. (141), 145° (144). Note, however, that $\bar{C}$ with KF in anhydrous formic acid gives (147) formyl fluoride, b.p. 26° at 750 mm. (147), while $\bar{C}$ with KF in AcOH gives (147) acetyl fluoride, b p. 20–22° (147).]

$\bar{C}$ with HBr. [$\bar{C}$ with dry HBr gas at 100° gives (148) benzoyl bromide [Beil. IX-195, IX_1-(95)], b.p. 218–219° cor. at 760 mm. (149), 215.0° at 741 mm. (150), 90–91° at 12 mm. (16), m.p. +8.1° (150), $D_4^{20} = 1.5461$ (150), $n_D^{20} = 1.5900$ (150).]

$\bar{C}$ with HI. [$\bar{C}$ with excess HI at ord temp. (148) (16), or $\bar{C}$ with Mg + I_2 in dry ether (151), gives benzoyl iodide [Beil. IX-195, IX_1-(95)], b.p. 109–109.5° at 10 mm. (148) cf. (16). Note that $\bar{C}$ with KI does *not* (152) give benzoyl iodide.]

$\bar{C}$ with metals. [$\bar{C}$ with Na in dry ether stood 10 days at room temp. gives (86% yield (153)) (154) ethyl benzoate (1:3721) but $\bar{C}$ with Na/Hg in dry ether causes the reaction to take a more complicated course (see above under reduction of $\bar{C}$). $\bar{C}$ with Na vapor gives (155) cf. (154) benzil (1:9015). $\bar{C}$ with K in xylene refluxed 2 days gives (153) benzoic anhydride (1.0595).]

[For behavior of $\bar{C}$ with Zn in dry ether or in di-isoamyl ether at 20–32° see (156). For behavior of $\bar{C}$ with finely divided Cu or Ni at elevated temps see above under pyrolysis of $\bar{C}$.]

$\bar{C}$ WITH VARIOUS METAL OXIDES OR SALTS

$\bar{C}$ with Na_2O_2. [$\bar{C}$ with Na_2O_2 in water at 5° (157) cf. (159) or $\bar{C}$ with 30% H_2O_2 + aq. NaOH (158) cf. (159) gives (yields: 91% (157), 60–70% (158)) benzoyl hydrogen peroxide

(perbenzoic acid) [Beil. IX-178, IX_1-(93)], m.p. 42°. For other methods for prepn. of perbenzoic acid such as from dibenzoyl peroxide with $NaOCH_3$ in $MeOH/CHCl_3$ (160) or with $NaOC_2H_5$ in EtOH/toluene (161), or from benzaldehyde in acetone with air (162), see indic. refs. For study of Na perbenzoate (157) and its use in purification (163) of perbenzoic acid see indic. refs.]

[$\bar{C}$ with Na_2O_2 in aq. at 0° (164) (165) or in aq. acetone (166), or $\bar{C}$ with aq. H_2O_2 + NaOH (167) or aq. H_2O_2 + iron-free $Ca(OH)_2$ (168), or $\bar{C}$ with aq. $BaO_2.8H_2O$ (169) (170) (171), or $\bar{C}$ with perbenzoic acid (see preceding paragraph) + aq. $NaHCO_3$ (172) gives dibenzoyl peroxide [Beil. IX-179, IX_1-(93)], m.p. 105°. For review of prepn. and properties of this prod. see also (173).]

$\bar{C}$ with misc. salts. $\bar{C}$ on warming with various inorganic salts yields benzoic anhydride. [E.g., $\bar{C}$ with $NaNO_2$ (174) cf. (175) (176), with KNO_3 (177), with $Pb(NO_3)_2$ (178), with nitrates of other heavy metals (179), with $Na_3PO_4.12H_2O$ in aq. soln. at 60° (180), with $K_2S_2O_5$ *in pyridine* (181), *with* Na_2SO_3 *in pyridine* (183) *in pres. of* C_6H_6 (181) *cf.* (182), or with BaO at 140–150° (184) gives benzoic anhydride (1:0595), m.p. 42°. For other methods of conversion of $\bar{C}$ to benzoic anhydride see above under pyrolysis of $\bar{C}$ and below under behavior of $\bar{C}$ with organic acids and their salts.]

$\bar{C}$ with NaN_3. [$\bar{C}$ with NaN_3 in aq. acetone at 0° (185), or in dry ether (186), gives (54.6% yield (185)) benzoyl azide (benzazide) [Beil. IX-332], m.p. 32° (185). Note that although this prod. readily explodes on htg. (187) (188) yet in inert solvents such as C_6H_6 (194) it smoothly decomposes into N_2 and phenyl isocyanate (for study of mechanism see (189)); under certain circumstances the latter may be hydrolytically split to aniline cf. (190). For studies on decomposition of benzoyl azide by ultrasonic waves see (185) (193).]

Hydrolysis of $\bar{C}$

$\bar{C}$ with cold aq. is slowly and with warm aq. rapidly hydrolyzed (105) to benzoic acid (1:0715) and HCl. [For study of rate of hydrolysis of $\bar{C}$ in ether with aq. at 20–22° (195) or at 0° (148), in 50% aq. acetone at 0° in pres. of H_2SO_4 (196) cf. (198), in various other organic solvents immiscible with aq. (197) or with $BaBr_2.2H_2O$ at 158° (199) see indic. refs.]

$\bar{C}$ with aq. alkali on warming readily yields (105) alkali benzoate + alkali chloride. Note that $\bar{C}$ in 50% aq. pyridine hydrolyzes much faster than in aq. NaOH or aq. Na_2CO_3 (39) (use in determination of atomic weight of carbon by hydrolysis of $\bar{C}$ and pptn. of AgCl (39)). Note that rate of hydrolysis of $\bar{C}$ is 2000 times as fast (200) as that of benzyl chloride (3:8535).

[Note that $\bar{C}$ in Ac_2O soln. behaves as an acid (201) and can be titrated (202) with NaOAc in Ac_2O.]

Behavior of $\bar{C}$ with Various Inorganic Sulfur Compounds

With H_2S. [The behavior of $\bar{C}$ with H_2S is disputed; on one hand $\bar{C}$ in dry pyridine treated with H_2S at 5° and subsequently acidified is claimed (203) to give thiolbenzoic acid, $C_6H_5.CO.SH$ [Beil. IX-419, IX_1-(169)] (see next paragraph); on the [illegible] $\bar{C}$ refluxed in dry pyridine in stream of H_2S is [illegible]d (204) to yield [illegible] ide $(C_6H_5.CS)_2O$, colorless cryst. from hot alc. [illegible]]

With KSH. [$\bar{C}$ with cold alc. KSH [illegible] KOH with H_2S [illegible]
(207) (209) (8) *salt of thiolbenzoic* [illegible] IX-419, [illegible]
(207) (208), b.p. 98.0–98.6° at 11–12 [illegible] 0.05 mm. (8[illegible]
that this product is readily [illegible] dibenzoyl dis[illegible]
by air or mild oxidizing ag[illegible] (35% aq. [illegible]
air followed by H_2O_2 as di[illegible] 5–10° [illegible]

in acetone followed by I_2/KI oxidn. (213), or with HSMgBr followed by air oxidn. (208) gives (65–70% yield (210)) dibenzoyl disulfide [Beil. IX-424], cryst. from 1,2-dichloroethane (3:5130) (210) (211) (212), m.p. 128–129° (210) (211) (212); this prod. has considerable pharmaceutical interest as an antipruritic; for hydrolysis to benzoic acid as method of detn. see (210) (214).]

Behavior of C̄ with Various Inorganic Nitrogen Compounds

With NH_3. [C̄ with conc. aq. NH_4OH (215), with dry NH_3 (105), with liq. NH_3 (216), with solid $(NH_4)_2CO_3$ (217), or with KNH_2 in dry ether (218) gives benzamide [Beil. IX-195, IX_1-(96)], m.p. 130°; note that either the $(NH_4)_2CO_3$ (219) or KNH_2 (218) methods may give also small amounts of *N*-benzoylbenzamide (dibenzamide) [Beil. IX-213, IX_1-(104)], m.p. 148°, and/or *N,N*-dibenzoylbenzamide (tribenzamide) [Beil. IX-214, IX_1-(104)], m.p. 207–208°. However, C̄ with NH_3 gas over Al_2O_3 at 490–500° gives (220) benzonitrile [Beil. IX-275, IX_1-(121)], b.p. 191°, m.p. −13°.]

With NH_2OH. [C̄ in C_6H_6 with free NH_2OH (221), or C̄ in C_6H_6 with $NH_2OH.HCl$ + pyridine (221), or C̄ in ether with $NH_2OH.HCl$ + Na_2CO_3 (221), gives benzohydroxamic acid (*N*-benzoylhydroxylamine) [Beil. IX-301, IX_1-(128)], cryst. from EtOAc, m.p. 128°. Note that C̄ with aq. NH_2OH solns. (222) also gives side reactions which diminish yield and increase difficulty of purification of prod.; also that C̄ with $NH_2OH.HCl$ in toluene gives (222) benzohydroxamic acid benzoate (dibenzohydroxamic acid) [Beil. IX-303, IX_1-(128)] and other products. For alternative method of prepn. of benzohydroxamic acid from ethyl benzoate (1:3721) with $NH_2OH.HCl$ + MeOH/KOH see (223); for review of utility of hydroxamic acids in org. qual. anal. see (224); for study of formn. of benzohydroxamic acid and its $FeCl_3$ color reaction as method of detn. of hydroxylamine see (230).]

With $NH_2.NH_2$. [C̄ (1 mole) with $N_2H_4.H_2O$ (2 moles) in ether gives (225) benzhydrazide (*N*-benzoylhydrazine) [Beil. IX-319, IX_1-(129)], m.p. 112°, but this prod. is usually better obtd. from reaction of $N_2H_4.H_2O$ with MeOBz (1:3586) (226) or EtOBz (1:3721) (227) (225). C̄ (1 mole) with $N_2H_4.H_2SO_4$ (0.5 mole) + aq NaOH (2.3 moles) as directed gives (66–75% yield (228)) *N,N'*-dibenzoylhydrazine [Beil. IX-324, IX_1-(131)], ndls. from AcOH (228) or EtOH (229), m.p. 237–238° (229).]

BEHAVIOR OF C̄ WITH ORGANIC REACTANTS

Behavior of C̄ with Hydrocarbons

With cycloalkanes. [C̄ with cyclohexane (1:8405) + $AlCl_3$ gives (19% yield (231)) phenyl 2-methylcyclopentyl ketone, b.p. 160–162° at 36 mm., $D_4^{18} = 1.0255$, $n_D^{18} = 1.5380$, accompanied by much benzaldehyde (1:0195) presumably formed from C̄ by the hydrogen corresp. to coupling of 2 moles of cyclohexane.]

With alkenes. [C̄ with ethylene + $AlCl_3$ in special apparatus as directed gives (87–92% yield (232)) phenyl β-chloroethyl ketone (β-chloropropiophenone) (3:1115); cf. also (233).]

With cycloalkenes. [C̄ with cyclohexene (1:8070) + $AlCl_3$ in CS_2 gives by addition phenyl 2-chlorocyclohexyl ketone (234), which on dehydrochlorination in the pres. of $AlCl_3$ (234) or with alc. KOH (235) gives (40% yield (235)) phenyl cyclohexenyl ketone (tetrahydrobenzophenone), b.p. 147° at 8 mm., $D_4^{22} = 1.070$, $n_D^{22} = 1.5595$ (235).]

With alkynes. [For behavior of C̄ with heptyne-1 (1:8085) in pres. of $AlCl_3$, $ZnCl_2$, $SnCl_4$, BF_3, etc., see (236).]

With aromatic hydrocarbons. [C̄ with C_6H_6 in pres. of $AlCl_3$ gives (yields: 74% (237), 71–74% (238)) (240) (241) (242) (243) (244) (245) benzophenone (1:5150), but best (239) prepn. of latter is from C_6H_6 + CCl_4 (3:5100) + $AlCl_3$. — For studies of substitution for

$AlCl_3$ of $FeCl_3$ (237) (238) (246) (247) (248), $FeCl_3 + AlCl_3$ (249), $GaCl_3$ (250), $TlCl_3$ (251), WCl_6 (252), UCl_4 (252), $ZrCl_4$ (253), Cr powder (254), $ZnCl_2$ (238), $SbCl_3$ (255) (256), or $SbBr_3$ (257) see indic. refs. — $\bar{C}$ with C_6H_6 in liq. HCl at 200° and 250 pounds press. (258) or in pres. of P_2O_5 in s.t. at 180–200° (259) (260) gives small yield of benzophenone (1:5150). — $\bar{C}$ with C_6D_6 + $AlCl_3$ in CS_2 gives (261) phenyl pentadeuterophenyl ketone, b.p. 160° at 15 mm. (corresp. oxime, m.p. 140°, does *not* depress m.p. of ordinary benzophenone oxime).]

[*$\bar{C}$ with toluene in pres. of $AlCl_3$ gives (262) (263) (264) mainly phenyl p-tolyl ketone* (1:5160) together with some phenyl *o*-tolyl ketone [Beil. VII-439, VII_1-(234)]. For studies of substitution for $AlCl_3$ of $FeCl_3$ (263), $FeCl_3 + AlCl_3$ (265), or $SbCl_3$ (255) (256) see indic. refs.]

[For reaction of $\bar{C}$ in pres. of $AlCl_3$ with *o*-xylene (1:7430) (262), *m*-xylene (1:7420) (262) (266) (267), *p*-xylene (1:7415) (262), ethylbenzene (268) (266) (269), see indic. refs.]

[$\bar{C}$ with biphenyl (1:7175) in pres. of $AlCl_3$ gives (yields: 75% (270), 60% (271)) (272) (273) (274) (275) (276) (242) phenyl *p*-xenyl ketone (*p*-phenylbenzophenone) [Beil. VII-521, VII_1-(290)], scales from alc., m.p. 106° cor. (270), 106° (272) (273), 102–103° (275), 102° (271) (274), 101–102° (242), 101° (276); b.p. 413° at 758 mm. (271), 419–420° at 744 mm. (274), 258° at 10 mm. (276) (corresp. oxime exists in two stereoisomeric forms (277), m.p. 200° and 173°, usual mixt. having m.p. 193–194° (278), 186–187° (271); corresp. 2,4-dinitrophenylhydrazone, m.p. 217–217.5° (271)); for use of P_2O_5 (instead of $AlCl_3$) in *prepn. of p-phenylbenzophenone (above) see (279). Note that the isomeric o-phenyl*benzophenone, m.p. 86–87°, has been prepared indirectly (280).]

[$\bar{C}$ with naphthalene (1:7200) in pres. of $AlCl_3$ in CS_2 (281) (282) (283) (284) (285) (286) or without solvent at 150° (286), or in liq. SO_2 (287), or $\bar{C}$ with naphthalene in pres. of $ZnCl_2$ at 125° (286) cf. (288) (289) or of P_2O_5 (289) (279) (259) (260), gives (yields: 85% (282), 52% (287)) mainly phenyl α-naphthyl ketone (1-benzoylnaphthalene) [Beil. VII-510, VII_1-(283)], pr. from alc., m.p. 75.5–76° (276), 75.5° (282), 75–76° (281), 75° (283), b.p. 386° at 764 mm. (284), 222° at 8 mm. (276); note that this prod. is usually accompanied by some phenyl β-naphthyl ketone (2-benzoylnaphthalene) [Beil. VII-511, VII_1-(283)], ndls. from alc., m.p. 82° (276) (289), 81–83° (281), b.p. 398° at 754 mm. (284), 225° at 8 mm. (276).]

[For reaction of $\bar{C}$ with anthracene (1:7285) + $AlCl_3$ in CS_2 (277) (290) (291) (292) (293), or in nitrobenzene at −10° (294), or without $AlCl_3$ in boiling nitrobenzene (295) giving (*yields: 85% (277), 78% (290)) 9-benzoylanthracene (α-anthraphenone)* [Beil. VII-538], cryst. from EtOAc, m.p. 145.5–146° (277), see indic. refs.; note, however, that for prepn. of this prod. use of benzoic anhydride (1:0595) (rather than $\bar{C}$) is preferred (296). — For reaction of $\bar{C}$ with phenanthrene (1:7240) + $AlCl_3$ in CS_2 (297) (298) or in nitrobenzene (298) see indic. refs.]

With heterocyclic parent nuclei. The behavior of $\bar{C}$ with furan (1:8015) in the pres. of Friedel-Crafts cat. has apparently not been reported [however, the prod. to be expected, viz., phenyl α-furyl ketone [Beil. XVII-348, $XVII_1$-(186)], b.p. 285° at 759 mm. (299), 186° at 46 mm. (299), 164° at 19 mm. (299), D_{-}^{20} = 1.1732 (300), D_{10}^{19} = 1.1839 (299), n_D^{20} = 1.6055 (299), *1.5798 (300), has been obtd. (49% yield (301)) from benzoic* anhydride (1:0595) with furan (1:8015) + $SnCl_4$ in C_6H_6, and from furoyl chloride (3:8515) with C_6H_6 in pres. of $AlCl_3$ (299).]

[$\bar{C}$ with thiophene in pres. of $AlCl_3$ (302), $SnCl_4$ (303) (304), P_2O_5 (305), or α-thienylmercuric chloride (306) cf. (307) (308) gives (yields: 89–90% (302), 82.5% (304)) phenyl α-thienyl ketone [Beil. XVII-348, $XVII_1$-(187)], m.p. 56° (305) (307), 55.5–56° (306), 55–56° (302), 55° (303) (304).]

Behavior of $\bar{C}$ with Organic Hydroxyl Compounds

$\bar{C}$ with organic OH or SH compounds (or their metallic salts) gives in general the corresponding benzoates. With phenols, however, there is also the additional possibility (according to the conditions employed) of either direct nuclear benzoylation or Fries rearrangement of the benzoate esters to give phenolic ketones.

Esterification of alcohols or phenols with $\bar{C}$ in presence of aqueous alkali comprises a general procedure first discovered by Lossen (309) and later developed and extended by Schotten, Baumann, and others. The reaction is not restricted to the use of benzoyl chloride but covers acid halides in general, e g, acetyl chloride, *p*-nitrobenzoyl chloride, 3,5-dinitrobenzoyl chloride, benzenesulfonyl chloride, etc

For detailed quantitative study of the influence of conditions on the Schotten-Baumann reaction see (310); *for study of its application to p-nitrobenzoyl chloride (311) or of* 3,5-dinitrobenzoyl chloride (312) in the derivatization of alcohols in dilute aqueous solution *see indic. refs.; for study of substitution of the acyl halide by the corresponding anhydride* see (313).

Note that in general the yield of ester is improved by use of low temperature (0°–25°) (310), by use of relatively concentrated solutions of both the hydroxyl compound and the *alkali (310), and sometimes by additions of NaOAc or other salts. (311).*

With monohydric alcohols. $\bar{C}$ with monohydric alcs. gives the corresponding alkyl benzoates.

[E.g., $\bar{C}$ with MeOH (1 6120) gives methyl benzoate (1.3586), b.p. 199.6°, m.p. −12.5° *(for study of rate of reaction at 0° and 25° see (18)).* — $\bar{C}$ with EtOH (1:6130) gives ethyl benzoate (1·3721), b p. 213.2°, m p. −34.2° (for study of rate of esterification at 0° (17) *or at 25° in various solvents (314)* see indic. refs. — $\bar{C}$ with *n*-PrOH (1·6150) gives *n*-propyl benzoate (3:3917), b.p. 231°. — $\bar{C}$ with isopropyl alc. (1.6135) gives isopropyl benzoate (1:3766), b p. 218.5° *(for study of rate of esterification at 25° (6) or at 30° (11) (315)* see indic. refs).]

[$\bar{C}$ *with n*-BuOH (1·6180) gives *n*-butyl benzoate (1·4104), b.p. 250.3°, *m.p.* −22.4°. — $\bar{C}$ with isobutyl alc (1:6165) gives isobutyl benzoate (1.4006), b p 242.2° cor. — $\bar{C}$ with *sec*-BuOH *(1:6155) gives (yields.* 75% (316), 66% (317), 20% (318)) *sec*-butyl benzoate [Beil. IX-112, IX_1-(63)], b.p. 234 5–235 5° cor. at 757 mm. (317), 148–151° at 50 mm. (317), 115–117° at 20° (319), 112–116° at 14 mm (318), D_4^{25} = 0 9945 (317), $n_D^{21.3}$ = 1.4933 (319). — $\bar{C}$ with *ter*-BuOH (1:6140) in pres. of pyridine gives (yields 86% (320), 80% (321) (322)) *ter-butyl benzoate [Beil.* IX_1*-(64)],* b.p. *112° at 18 mm. (321), 91–92° at 8 mm. (323),* 91.3° at 7.5 mm. (320), 96° at 2 mm. (322); D_4^{25} = 0.9928 (322); n_D^{25} = 1.4896 (322) (321), n_D^{20} = 1.4910 (320).]

[$\bar{C}$ with *n*-AmOH (1:6205) gives *n*-amyl benzoate [Beil. IX_1-(64)], b.p. 138–139° at 15 mm (316), 137–138° at 15 mm. (324). — $\bar{C}$ with isoamyl alc. (1:6200) gives isoamyl benzoate (1:4166), b.p. 262.3° cor. at 760 mm. — $\bar{C}$ with neopentyl alc. (1:5812) gives (325) neopentyl benzoate, b.p. 235–237° at 740 mm., 110–111° at 10 mm., D_{25}^{25} = 0.9817, n_D^{25} = 1.4875 (325).]

$\bar{C}$ reacts with other alcohols and thiols similarly, but details cannot be tabulated here.

With phenols. $\bar{C}$ can react with phenols in either or both of two modes; on one hand it can benzoylate the phenolic OH yielding the corresponding phenol benzoates (a list of the melting points of 88 phenols of Order 1 is given on page 638 of Vol. I of this series (326); for study of effect of structure on rate of benzoylation of various monohydric phenols see (329)); on the other hand $\bar{C}$ may under certain conditions effect the direct nuclear benzoylation of phenols. Since the phenolic ketones thus formed may also be more or less readily obtained by catalyzed rearrangement of the phenol benzoates, the chemistry of the phenol

benzoates and their rearrangement products is so voluminous that it cannot here be given detailed discussion. [For extensive reviews of the Fries rearrangement (327) (328) of phenol esters (including the benzoates) see indic. refs.]

With enols (or their metallic derivatives). *With methyl acetoacetate.* [C̄ with the Na enolate of methyl acetoacetate (1:1705) gives (330) methyl α-benzoylacetoacetate, b.p. 136–137° at 2 mm. (corresp. Cu enolate, blue-green ndls. from dioxane, m.p. 226–228°; corresp. semicarbazone, prepd. by indirect means, m.p. 166° (331)).]

With ethyl acetoacetate. [C̄ with the Na enolate of ethyl acetoacetate (1:1710) gives (yields: 74.8% (332), 67% (333), 63–75% (334) cf. (335) (337) ethyl α-benzoylacetoacetate [Beil. X-817, X_1-(396)], b.p. 202° at 50 mm. (335), 177–181° at 20 mm. (334), 175–176° sl. dec. at 12 mm. (337), 169° sl. dec. at 11 mm. (338), 165–167° at 10 mm. (333) (corresp. Cu enolate, m.p. 224° (336), 221–222° (339)). Note that this prod. upon cleavage of the acetyl group, e g, with aq. $NH_4OH + NH_4Cl$, gives (77–78% yield (334)) (332) ethyl benzoylacetate (1:1778), for alternative prepn. of which see (340). — Note, however, that two forms of the isomeric ethyl *O*-benzoylacetoacetate are known (341); a liq. form, b p. 153–155° at 3 mm., prepd. from ethyl acetoacetate (1:1710) with C̄ + pyridine, and a solid form, m.p. 42°, prepd. from the Cu enolate of ethyl acetoacetate (1:1710) with C̄ in ether (for much further detail see (341)).]

With acetylacetone. [C̄ with the Na enolate (342) or K enolate (343) of acetylacetone (1:1700) in ether gives (50% yield (343)) *C*-benzoylacetylacetone (α-benzoyl-α-acetylacetone) [Beil. VII-865, VII_1-(474)], m.p. 35° (342), 34–35° (343), b.p. 167° at 22 mm. (342), accompanied by some of the higher-melting form, m.p. 103° (342), 102–103° (343), of its benzoate [Beil. IX-156]; note that the lower-melting form, m.p. 66–67° (344), is obtd. from α-benzoyl-α-acetylacetone (above) with C̄ in pyridine (344).]

With benzoylacetone. [C̄ with Na enolate of benzoylacetone (1:1450) under various conditions gives (345) (346) (347) cf. (348) α,α-dibenzoylacetone [Beil. VII-872, VII_1-(480)] (q.v. for constants of various enol and keto forms) and/or the corresp. benzoate [Beil. IX-157], m.p. 87–88° (349).]

With dibenzoylmethane. [C̄ with Na enolate of dibenzoylmethane (1:1480) gives (45% yield (350)) (351) (352) (353) tribenzoylmethane [Beil. VII-877, VII_1-(485)] (q.v. for constants of various forms) and/or the corresp. benzoate [Beil. IX-158], m.p. 121–122° (351).]

Behavior of C̄ with Ethers

With aliphatic ethers. Acyl chlorides with aliphatic ethers do not react even at elevated temperatures (354) although acid bromides (e.g., acetyl bromide (355)) or acyl iodides (e.g., benzoyl iodide (356)) are able to effect cleavage into alkyl halides and alkyl esters. However, when acyl chlorides are heated with aliphatic ethers in the presence of certain metallic salts, cleavage of the ethers is more or less readily effected. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

[C̄ with diethyl ether (1:6110) on htg. in pres. of $ZnCl_2$ (354) (357) (358) (359) (360), $SnCl_4$ (358), $ZrCl_4$ (358), $TiCl_4$ (358) (362), $SbCl_5$ (358), $FeCl_3$ (358) (361), $AlCl_3$ (358) (362), or $SbCl_3$ (358) gives ethyl benzoate (1:3721); note, however, that use of BF_3, $CuCl_2$, and $SnCl_2$ gives only traces while $SiCl_4$, PCl_3, PCl_5, BCl_3, $AsCl_3$, or $MgCl_2$ achieves no cleavage (358) of the ether. Note that by extension of the $ZnCl_2$ method to use of 3,5-dinitrobenzoyl chloride a procedure for the identif. of ethers as the corresp. alkyl 3,5-dinitrobenzoates has been described (363) cf. (364).]

With phenol ethers. With phenol ethers where no phenolic OH remains to interfere, C̄ reacts in the pres. of suitable cat. in the Friedel-Crafts sense. Although the topic cannot here be pursued exhaustively, several examples are cited in the following text.

[$\bar{C}$ with methyl phenyl ether (anisole) (1:7445) + $AlCl_3$ in CS_2 solution (81% yield (365)) (366) (367) cf. (368) (360) or without other solvent (369) gives mainly *p*-anisyl phenyl ketone (*p*-methoxybenzophenone) (1:5170), m p. 62° (366) (367) (370), 61–62° (365) (369), 61° (371), b.p. 354–355° at 729 mm. (371); this prod. is accompanied by some *o*-anisyl phenyl ketone (*o*-methoxybenzophenone) (1:5142), m.p. 39°, which is separable from the main prod. only by repeated recrystallization from lgr. (b.p. 40–60°) and alc. (369).]

[$\bar{C}$ with ethyl phenyl ether (phenetole) (1.7485) + $AlCl_3$ in CS_2 soln. (yields: 83% (372), 73% (374)) (369) (366) (373) or without other solvent (369) gives mainly *p*-phenetyl phenyl ketone (*p*-ethoxybenzophenone) [Beil. VIII-159, $VIII_1$-(569)], m.p. 47–48° (374), 47° (369) (372), 46.5° (373), 38–39° (366), b.p. 245–250° at 25 mm. (374), 227° at 21 mm. (373), 215–225° at 15 mm. (373) (corresp. oxime, m.p. 135–136° (374)), accompanied by some *o*-phenetyl phenyl ketone (*o*-ethoxybenzophenone) which (although not further characterized) is liq. and readily separable.]

[$\bar{C}$ with diphenyl ether (1:7125) + $AlCl_3$ in CS_2 (375) (376) (374), or $\bar{C}$ with diphenyl ether (1:7125) + $HgCl_2$ at 150–160° (377) (27% yield), or $\bar{C}$ with phenyl 4-chloromercuriphenyl ether at 150° (377), gives (yields: 97% (375), 95% (374), 70% (377)) *p*-phenoxybenzophenone [Beil. VIII-159], m.p. 71° cor. (375), 70–71° (374), 66° (377) (corresp. oxime, m.p. 124° (374)); for further benzoylation of this prod. to *bis*-(*p*-benzoylphenyl) ether, m.p. 163–164°, see (376).]

[$\bar{C}$ with methyl α-naphthyl ether (1:7630) + $AlCl_3$ in CS_2 (378) or in nitrobenzene (379) gives (84% yield (379)) 4-benzoyl-1-methoxynaphthalene, m.p. 82–83° (378), 81–82° (379); for high-press. hydrogenation of this prod. giving (84–86% yield) 4-benzyl-1-methoxynaphthalene, m.p. 83–84°, see (379). — $\bar{C}$ with methyl β-naphthyl ether (1:7180) + $AlCl_3$ in CS_2 gives (85% yield (380)) 1-benzoyl-2-methoxynaphthalene, m.p. 125° cor.; note that use of 1,1,2,2-tetrachloroethane as solvent is much less satisfactory (381). — $\bar{C}$ with ethyl α-naphthyl ether (1:7635) + $AlCl_3$ in CS_2 gives (366) (382) 4-benzoyl-1-ethoxynaphthalene [Beil. VIII-207, $VIII_1$-(586)], m.p. 74–75° (366), accompanied (383) by some 4-benzoylnaphthol-1 and other products. — The presumably analogous reaction of $\bar{C}$ with ethyl β-naphthyl ether (1:7135) + $AlCl_3$ appears not to have been studied, and the expected 1-benzoyl-2-ethoxynaphthalene is unreported.]

Behavior of $\bar{C}$ with Acids (or Their Salts)

With sodium formate. [$\bar{C}$ with NaOOCH on htg. (384) gives BzOH (1:0715), CO, + HCl.]

With acetic acid. [$\bar{C}$ with AcOH (1:1010) refluxed in pres. of charcoal (385), or in pres. of a tertiary base (386) even at ord. temp., or $\bar{C}$ with NaOAc on warming (387) cf. (388) (389) gives the mixed anhydride, $CH_3.CO.O.CO.C_6H_5$ [Beil. IX-163], accompanied by various other products. Note, however, that $\bar{C}$ with AcOH (1:1010) at 100° for 3 hrs. gives (70% yield (147)) acetyl chloride (3:7065) while $\bar{C}$ with Ac_2O (1:1015) at 100° for 1 hr. gives (77% yield (147)) acetyl chloride (3:7065) accompanied by benzoic anhydride (1:0595). For prepn. of acetic-benzoic anhydride by other means, e.g., from benzoic acid (1:0715) with ketene (390), and for study of its use in Friedel-Crafts type reactions (391), see indic. refs.]

With benzoic acid. [$\bar{C}$ with benzoic acid (1:0715) in s t. at 160–200° for 12 hrs. (392), or at 220° under reduced press. (397), or with pyridine (389) (393), or $\bar{C}$ with NaOBz shaken with aq. (394) or htd. at 130° (395), gives benzoic anhydride (1:0595), m.p. 42°, b.p. 360°; for other modes of formn. of this prod. from $\bar{C}$ see above under behavior of $\bar{C}$ with various inorganic salts; for prepn. (72–74% yield) of benzoic anhydride (1:0595) from benzoic acid (1:0715) by use of acetic anhydride (1:1015) see (396).]

With HCN. [$\bar{C}$ with dry [illegible] with HgCN (400) (401) (403) (404), AgC[illegible] –65% (12)) benzoyl cyanide (phenylgly[illegible] 34° (401), 32.5–34° (403), 32–33° (12), b.p. 208–209° at 745 mm. (12), 207–210° (402), 206–208° (404), 123° at 42 mm. (401), 99° at 19 mm. (405). Note that by the HCN/pyridine method (398) (399) (406) or by reaction of $\bar{C}$ with aq. KCN (402) *dimeric* benzoyl cyanide [Beil. XIX-362], m.p. 99–100° (402), 95–96° (406), is also formed; further that benzoyl *bromide* with AgCN gives (402) a *trimeric* benzoyl cyanide, m.p. 195°.]

With cyanate or thiocyanate salts. [$\bar{C}$ with K cyanate (407), KSCN (408), or NH_4SCN (409) gives benzonitrile [Beil. IX-275, IX_1-(121)], b.p. 191.3° at 760 mm., but $\bar{C}$ with $Pb(SCN)_2$ at 160° (410), at 120° (413), or refluxed in C_6H_6 (411) (412) gives benzoyl isothiocyanate [Beil. IX-222, IX_1-107], b.p. 119° at 10 mm. (412), $D_4^{18.3} = 1.2142$ (412), $n_D^{18.3} = 1.6382$ (412).]

Behavior of $\bar{C}$ with Organic Nitrogen Compounds

$\bar{C}$ reacts with primary and secondary amines to replace one of the amino hydrogen atoms by the benzoyl radical. The molecule of HCl thus split out will, of course, convert a second molecule of amine to its hydrochloride. In order to avoid this waste of amine, the benzoylation may be effected in the presence of aqueous alkali (Schotten-Baumann reaction) or of pyridine (Einhorn reaction). Since the number of amino compounds which undergoes benzoylation is legion, the present text will be restricted to a relatively few important cases.

With aliphatic primary amines. [$\bar{C}$ with aq. CH_3NH_2 (414) in pres. of alk. (415) gives *N*-methylbenzamide [Beil. IX-201, IX_1-(97)], cryst. from alc. (416), aq. (417), or lgr./C_6H_6 (418), m.p. 82° (416), 80–81° (418) (419), 79.8° (417), 79° (414), 78° (415), b.p. 291° at 765 mm. (419), 167° at 11 mm. (420). — $\bar{C}$ with aq. $C_2H_5NH_2$ (414) gives *N*-ethylbenzamide [Beil. IX-202, IX_1-(97)], ndls. from aq., m.p. 71° (419), 70° (421), 69° (417), 68–69° (414), 67° (420), b.p. 285° at 745 mm. (419). — $\bar{C}$ with n-$C_3H_7NH_2$ presumably yields *N*-(*n*-propyl)benzamide [Beil. IX-203, IX_1-(97)], cryst. from alc. or C_6H_6, m.p. 84.5° (419), 83° (422), b.p. 294–295° sl. dec. (422), but this product has been reported only by other methods (419) (422). — $\bar{C}$ with n-$C_4H_9NH_2$ presumably gives *N*-(*n*-butyl)benzamide but this product has been characterized only as an oil cf. (423). — $\bar{C}$ with isobutylamine + aq. NaOH (416) cf. (424) gives *N*-(isobutyl)benzamide [B[illegible] ndls. from C_6H_6[illegible] $CHCl_3$, alc., or lgr.), m.p. 57–58° (416), 57° (419), 55[illegible] at 760 mm. (419), 173–178° at 13 mm. (416). — $\bar{C}$ [illegible] butyl)benzamide but the *d,l*-form of this product is unreported; note that its dextrorotatory form has been reported as m.p. 92° (425) or 86–88° (426); the levorotatory form as m.p. 88–89° (425). — $\bar{C}$ with *ter*-$C_4H_9NH_2$ in ether (427) (428) gives *N*-(*ter*-butyl)benzamide [Beil. IX_1-(97)], ndls. from ether/C_6H_6, m.p. 136.5° (428), 135.5° (427), 134–135° (429), 134° (430). Note that dibenzoylation does *not* occur and that *N*-methyldibenzamide [Beil. IX_1-(104), m.p. 94–95° (435), and *N*-ethyldibenzamide [Beil. IX-214], m.p. 101–102° (436), have been prepared only by indirect means.]

With aliphatic secondary amines. [$\bar{C}$ with $(CH_3)_2NH$ in ether (431), in aq. (414), or in aq. NaOH (405) gives *N,N*-dimethylbenzamide [Beil. IX-201, IX_1-(97)], cryst. from CS_2/pet. ether (405), m.p. 43° (405), 41–42° (431), 41° (414), b.p. 272–273° (420), 265–266° (432), 132–133° at 15 mm. (432). — $\bar{C}$ with $(C_2H_5)_2NH$ in ether (431) gives *N,N*-diethylbenzamide [Beil. IX-202], liquid, b.p. 280–282° cor. (431), 278–282° (433), 173–175° at 35 mm. (434). — Note that the analogous *N,N*-dialkylbenzamides to be expected from reaction of $\bar{C}$ with di-*n*-propylamine, di-isopropylamine, di-*n*-butylamine, di-isobutylamine, di-*sec*-butylamine, and di-*ter*-butylamine have not been characterized.]

With aromatic primary amines. See below under Ⓓ's.

With aromatic secondary amines. $\bar{C}$ with aromatic secondary amines gives the corresponding *N*-benzoyl derivatives but note that these same products are frequently also obtained by reaction of $\bar{C}$ with the appropriate tertiary amines.

[$\bar{C}$ with *N*-methylaniline (437), or $\bar{C}$ with *N,N*-dimethylaniline at 190° (438), gives *N*-benzoyl-*N*-methylaniline (*N*-methylbenzanilide) [Beil. XII-269], scales from lgr., m.p. 63° (438), 59° (437), b.p. 331–332° (439) — $\bar{C}$ with *N*-ethylaniline (not actually reported) or $\bar{C}$ with *N,N*-diethylaniline at 200° (438) gives *N*-benzoyl-*N*-ethylaniline (*N*-ethylbenzanilide) [Beil. XII-270], cryst. from ether + lgr., m.p. 54° (440), 52° (441), 60° (438).]

[$\bar{C}$ with *N*-methyl-*o*-toluidine should yield *N*-benzoyl-*N*-methyl-*o*-toluidine (*N*-methylbenzo-*o*-toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 65–66°, and $\bar{C}$ with *N*-ethyl-*o*-toluidine should yield *N*-benzoyl-*N*-ethyl-o-toluidine (*N*-ethyl-benzo-*o*-toluidide) [Beil. XII-796], pr. from ether/lgr., m.p. 71–72°, but both these products have been reported only by indirect means (442) — The analogous products to be expected from $\bar{C}$ with *N*-methyl (or *N*-ethyl)-*m*-toluidine, or $\bar{C}$ with *N*-methyl (or *N*-ethyl)-*p*-toluidine, have not been characterized in the literature.]

[$\bar{C}$ with *N*-methyl-α-naphthylamine should yield *N*-benzoyl-*N*-methyl-α-naphthylamine [Beil. XII-1234], cryst. from C_6H_6/lgr., m.p. 121°, but this prod. has actually been reported only from $\bar{C}$ with *N,N*-dimethyl-α-naphthylamine at 170–190° (438). — Similarly, $\bar{C}$ with *N*-methyl-β-naphthylamine + aq. alk. yields (443) *N*-benzoyl-*N*-methyl-β-naphthylamine [Beil. XII-1287, XII_1-(539)], ndls. from pet. eth., m.p. 84° (443); this prod. is also claimed (438) from *N,N*-dimethyl-β-naphthylamine at 170–180° but the m.p. of 169° is not in accord with the later work under mild conditions and presumably represents an isomeric material. — The analogous benzoyl derivatives of *N*-ethyl-α-naphthylamine and of *N*-ethyl-β-naphthylamine are unreported.]

[$\bar{C}$ with diphenylamine on warming (444) in ether soln. (445) gives *N*-benzoyldiphenylamine (*N,N*-diphenylbenzamide) [Beil. XII-270, XII_1-(201)], cryst. from alc., m.p. 180° (435), 179–180° (446), 177° (447).]

$\bar{C}$ with heterocyclic secondary amines. $\bar{C}$ with piperidine [Beil. XX-6, XX_1-(5)] directly (536) or better in aq. NaOH (537) (538) (539) gives (87–91% yield (537)) *N*-benzoylpiperidine [Beil. XX-46, XX_1-(15)], m.p. 49° (540), 48° (538), 44° (537); b.p. 320–321° (541), 240–244° at 130 mm. (537), 195° at 25 mm. (541), 180–184° at 20 mm. (537), 172–174° at 12 mm. (537); not volatile with steam (538). [Note that this prod. with PBr_5 (542) (543) (544) (545) (546), with $PBr_3 + Br_2$ (547), or with $PCl_3 + Br_2$ (548) comprises an important method of preparation of pentamethylene dibromide (1,5-dibromopentane).]

$\bar{C}$ with morpholine [Beil. XXVII-5] in ether gives (549) *N*-benzoylmorpholine, eas. sol. aq., pr. from dry ether, m.p. 74–75° (549).

$\bar{C}$ with aromatic diamines. [$\bar{C}$ with *o*-phenylenediamine [Beil. XIII-6, $XIII_1$-(5)] in aq. NaOH (448), or $\bar{C}$ with *o*-phenylenediamine hydrochloride in aq. soln. (449), gives *N,N'*-dibenzoyl-*o*-phenylenediamine [Beil. XIII-21, $XIII_1$-(8)], ndls. from AcOH, m.p. 301° (450), about 300° dec. (451) — Note that this prod. on htg. above m.p. (450), or on htg. with conc. HCl in s.t. at 200° (449), gives 2-phenylbenzimidazole [Beil. XXIII-230, $XXIII_1$-(61)], m.p. variously reported around 290°, which latter, although stable toward $\bar{C}$ at 260° (452), yet with $\bar{C}$ + aq. NaOH in cold (450) reverts to *N,N'*-dibenzoyl-*o*-phenylenediamine (above). — Note that *N*-benzoyl-*o*-phenylenediamine [Beil. XIII-20, $XIII_1$-(8)], m.p. 140° (453), has been reported only by indirect means (453) (454); on htg. 2 hrs. at 140° followed by a few minutes at 280° (455) it gives 2-phenylbenzimidazole (see above). — Note finally that 1-benzoylbenzimidazole [Beil. XXIII-133, $XXIII_1$-(35)], m.p. 93–94° (456), 91–92° (450), on htg. with $\bar{C}$ (457), or benzimidazole itself with $\bar{C}$ + aq. NaOH (450), both give *N,N'*-dibenzoyl-*o*-phenylenediamine (above).]

[$\bar{C}$ with hydrochloride of *m*-phenylenediamine [Beil. XIII-33, $XIII_1$-(10)] on htg. gives

(458) *N,N'*-dibenzoyl-*m*-phenylenediamine [Beil. XIII-46], ndls. from AcOH, m.p. 240° (458) (460); for behavior of this prod. with PCl_5 see (459). — Note that *N*-benzoyl-*m*-phenylenediamine (benz-*m*-aminoanilide) [Beil. XIII-46], m.p. 125°, has been reported only by indirect means (461) (462) (464).]

[$\bar{C}$ with *p*-phenylenediamine [Beil. XIII-61, $XIII_1$-(18)] + aq. NaOH (448) cf. (463) gives *N,N'*-dibenzoyl-*p*-phenylenediamine [Beil. XIII-98], m.p. above 300° (448) cf. (460); for behavior of this prod. with PCl_5 see (459). — Note that *N*-benzoyl-*p*-phenylenediamine (benz-*p*-aminoanilide) [Beil. XIII-98, $XIII_1$-(31)], m.p. 128° (452) (464), has been reported only by indirect means (452) (464).]

$\bar{C}$ with aminophenols. $\bar{C}$ with *o*-aminophenol [Beil. XIII-354, $XIII_1$-(108)] gives according to circumstances one of the two possible monobenzoyl derivatives, viz., *o*-(benzoylamino)phenol [Beil. XIII-372, $XIII_1$-(115)] (or its ring-closure product, 2-phenylbenzoxazole-1,3 [Beil. XXVII-72, $XXVII_1$-(235)]), or the dibenzoyl derivative, viz., *o*-benzoylaminophenyl benzoate [Beil. XIII-373], as more fully described below. Note, however, that the other monobenzoyl derivative of *o*-aminophenol, viz., *O*-benzoyl-*o*-aminophenol or *o*-aminophenyl benzoate, known only as its hydrochloride, m.p. 149° (465), has been prepared only by indirect means (465) viz., from *O,N*-(dibenzoyl)-*o*-aminophenol, and on heating, or even on recrystn., loses HCl giving (465) 2-phenylbenzoxazole-1,3.

[$\bar{C}$ (1 mole) with *o*-aminophenol (2 moles) in dry ether (466) gives *o*-(benzoylamino)-phenol (*N*-benzoyl-*o*-aminophenol), tbls. from MeOH (465), lfts. from C_6H_6, m.p. 169–171° u.c. (465), 169° (467), 167° (468) (corresp. acetate, m.p. abt. 140° (469) cf. (470); corresp. benzoate, m.p. 182° (470) (also below); corresp. benzenesulfonate, m.p. 90.5–91.0 (471)). — Note that this prod. on htg. above m.p. loses H_2O with ring closure yielding (468) 2-phenylbenzoxazole-1,3, m.p. 103° (see below). — Note also that *o*-(benzoylamino)phenyl benzoate (above) with $\bar{C}$ in nitrobenzene refluxed 12 hrs. gives (479) *o*-(dibenzoylamino)phenyl benzoate, m.p. 170.5–171.5° (479).]

[$\bar{C}$ with *o*-aminophenol on warming, followed by distn. of reaction product (472), or $\bar{C}$ with *o*-aminophenol hydrochloride (468) (473) gives 2-phenylbenzoxazole-1,3, ndls. from dil. alc., lfts. from dil. HCl or dil. H_2SO_4, m.p. 103° (468) (472) (473) (474), volatile with steam, b.p. 314–317° (472) (corresp. $\bar{B}$.PkOH, m.p. 104° (477), corresp. MeI quaternary salt, m.p. 196° dec. (478)).]

[$\bar{C}$ (2 pts.) with *o*-aminophenol in aq. NaOH (448) or in pyridine + $CHCl_3$ (465), or $\bar{C}$ with *o*-aminophenol hydrochloride in C_6H_6 at 100° (468), or $\bar{C}$ + aq. NaOH with *o*-formylaminophenol (480), *o*-(acetylamino)phenol (481), or *o*-(benzoylamino)phenol (467), gives *O,N*-dibenzoyl-*o*-aminophenol (*o*-benzoylaminophenyl benzoate), ndls. from alc. (480) or EtOAc (465), m.p. 185° (467), 183–184.5° (480), 182–183° (482), 181–182° (476), 180° (481), 179° u.c. (465). — Note that this prod. on boilg. with aq. $BaCO_3$ (468) or for 2 days with alc. HCl (483) hydrolyzes at the ester leakage giving *o*-(benzoylamino)phenol, m.p. 169° (above).]

[$\bar{C}$ with *m*-aminophenol [Beil. XIII-401, $XIII_1$-(128)] in pyridine + ether (484) cf. (485) gives *m*-(benzoylamino)phenol [Beil. XIII-416], ndls. from toluene, m.p. 174° (485) (486), 173° (484). — Note that the isomeric *O*-benzoyl-*m*-aminophenol (*m*-aminophenyl benzoate) is unreported. — $\bar{C}$ with *m*-aminophenol in aq. NaOH gives (486) *O,N*-dibenzoyl-*m*-aminophenol (*m*-(benzoylamino)phenyl benzoate) [Beil. XIII-416], pr. from C_6H_6 or scales from abs. alc., m.p. 153° (486); this product with boilg. alc. KOH splits at the ester linkage giving (486) *m*-(benzoylamino)phenol (above), m.p. 174°.]

[$\bar{C}$ with *p*-aminophenol [Beil. XIII-427, $XIII_1$-(143)] in aq. NaOH (487), in pyridine (488), in alc. (489), or in ether + aq. NaOH (490) gives *p*-(benzoylamino)phenol (*N*-benzoyl-*p*-aminophenol) [Beil. XIII-469, $XIII_1$-(165)], cryst. from AcOH, m.p. 216–217° (487), 214–215° (489) (for review of earlier confusion see (487)). — Note that the isomeric *O*-

benzoyl-p-aminophenol (p-aminophenyl benzoate) [Beil. XIII-440], m.p. 153–154° (491) (492), 148° (465), has been reported only by indirect means. — $\bar{C}$ with p-aminophenol on htg. (472), or in aq. NaOH (448) (487) (488) or in pyridine (488), or $\bar{C}$ with p-aminophenol hydrochloride (489) gives O,N-dibenzoyl-p-aminophenol (p-(benzoylamino)phenyl benzoate) [Beil. XIII-470, $XIII_1$-(165)], cryst. from MeOH, EtOH, AcOH, or xylene, m.p. 235° (487) (467), 233–234° (489), 231° (472).]

The acylation of aminophenols (especially of the ortho series) and the relationships of the various multiple and mixed acyl derivatives have been extensively studied by Raiford ((493)–(511), incl.), Nelson ((512)–(517), incl.), and Bell (518) (519); the cited papers are arranged in chronological sequence for each worker.

$\bar{C}$ with tertiary amines. $\bar{C}$ with certain tertiary amines especially in dry ether solution (520) forms addition products; these are presumably quaternary ammonium salts but have been very inadequately studied cf. (524).

[$\bar{C}$ with Me_3N in ether at 0° or in C_6H_6 at 80° fails to react (525). — $\bar{C}$ with Et_3N in dry ether gives an immediate ppt. which increases on stdg. but appears to be a mixture of the expected addn. prod., $\bar{C}.Et_3N$, with triethylamine hydrochloride (520). — $\bar{C}$ with triamylamine in dry ether after stdg. 2 months yields (520) long needles, m.p. 117°, whose analysis is in accord with "nearly pure" addn. prod., $\bar{C}.(C_5H_{11})_3N$.]

[$\bar{C}$ with N,N-dimethylaniline in dry ether in sunlight gives gradually hygroscopic crystals probably comprising the expected addn. prod., $\bar{C}.C_8H_{11}N$, (520). — $\bar{C}$ with N,N-diethylaniline in dry ether gives (520) a crystn. prod. containing 71% of the expected $\bar{C}.C_{10}H_{15}N$.]

[$\bar{C}$ with pyridine in dry ether gives (520) a ppt. apparently contg. only 31% of the expected addn. prod., $\bar{C}.C_5H_5N$. — $\bar{C}$ with pyridine in C_6H_6 gives (521) pyridine hydrochloride, m.p. 144°. — For study of $\bar{C}$ with pyridine in pres. of Zn dust giving the free radical N-benzoylpyridinium see (522); for study of $\bar{C}$ with pyridine + N,N-dimethylaniline + Cu powder at 100° for 5 hrs. giving 4-(p-dimethylaminophenyl)pyridine see (523).]

Note that $\bar{C}$ with pyridine in pres. of various inorganic salts gives benzoic anhydride; for further details see text above under behavior of $\bar{C}$ with miscellaneous inorganic salts.

$\bar{C}$ with arylhydrazines. $\bar{C}$ (1 mole) with phenylhydrazine (2 moles) [Beil. XV-67, XV_1-(23)] in dry ether gives (526) N'-benzoyl-N-phenylhydrazine (also known as *sym.*-benzoylphenylhydrazine or β-benzoylphenylhydrazine) [Beil. XV-255, XV_1-(67)], pr. from alc., m.p. 168° (526) (527). [Note that the isomeric N-benzoyl-N-phenylhydrazine (also known as *asym.*-benzoyl-phenylhydrazine or α-benzoyl-phenylhydrazine) [Beil. XV-250, XV_1-(65)], m.p. 70°, has been obtained only by indirect means, e.g., from $\bar{C}$ with sodio-phenylhydrazine (528) or from N-chlorobenzanilide with $NaNH_2$ (529). However, $\bar{C}$ with phenylhydrazine hydrochloride in boilg. C_6H_6 (530) (531), or $\bar{C}$ with dry K phenylhydrazine-β-sulfonate on htg. (526), or $\bar{C}$ with α-benzoyl-phenylhydrazine in ether (532), or $\bar{C}$ with β-benzoylphenylhydrazine on htg. (526), gives N,N'-dibenzoyl-N-phenylhydrazine (also called α,β-dibenzoyl-phenylhydrazine) [Beil. XV-261, XV_1-(68)], pr. from alc., m.p. 177–178° (526) (530); note that this prod. on hydrolysis with alc. NaOH gives (533) β-benzoyl-phenylhydrazine (above).]

$\bar{C}$ with p-nitrophenylhydrazine [Beil. XV-468, XV_1-(130)] presumably gives N'-benzoyl-N-(p-nitrophenyl)-hydrazine [Beil. XV-479, XV_1-(140)], ndls. from alc., m.p. 193° (534), although this prod. is actually reported (534) only from benzoic anhydride (1:0595) with p-nitro-phenylhydrazine.

$\bar{C}$ with 2,4-dinitrophenylhydrazine [Beil. XV-489, XV_1-(146)] in alc. suspension on warming gives (535) N'-benzoyl-N-(2,4-dinitrophenyl)-hydrazine [Beil. XV-492], or.-red lfts. from alc., m.p. 206–207° (535).

$\bar{C}$ with diazomethane. [$\bar{C}$ added slowly to excess CH_2N_2 in ether at 0° gives (550) (551) (552) (553) ω-diazoacetophenone [Beil. VII-362, XXIV-142]; this product may be caused

to undergo the Wolff rearrangement giving (554) phenylacetoacetic acid derivs. (e.g., amide or anilide (554)), or may be caused to react with HCl to give phenacyl chloride (3:1212): for comprehensive survey and review of the behavior of acyl halides with diazomethane see (555).]

C̄ with miscellaneous nitrogen compounds. [For studies on the behavior of C̄ with indigo see (556) (557) (558) (559) (560) (561) (562) (563).]

Behavior of C̄ with Organometallic Compounds

Behavior of C̄ with Grignard reagents. C̄ with excess RMgX compounds in ether reacts in general to give the corresponding tertiary alcohols. Although extensive discussion of this reaction is manifestly infeasible here, the following examples are cited.

[C̄ with excess MeMgI gives (564) dimethyl-phenyl-carbinol [Beil. VI-506, VI_2-(477)]. — C̄ with EtMgI gives (93% yield (565)) diethyl-phenyl-carbinol [Beil. VI-548, VI_1-(269), VI_2-(506)]. — C̄ with n-PrMgBr gives (81% yield (565)) di-n-propyl-phenyl-carbinol [Beil. VI_1-(273), VI_2-(513)]. — C̄ with C_6H_5MgBr as directed gives (91.5% yield (565)) triphenylcarbinol [Beil. VI-713, VI_1-(349), VI_2-(686)] (1:5985) accompanied by (7% yield (565)) biphenyl (1:7175); for study of limiting reaction of C̄ with C_6H_5MgBr to formation of diphenyl ketone (benzophenone) (1:5150) see (566); note also that C̄ with C_6H_5MgBr in presence of $CoCl_2$ takes a different course yielding (567) benzoic acid, ethyl benzoate, biphenyl, benzophenone, phenylbenzoin, tetraphenylethylene oxide, and stilbene dibenzoate.]

[For interference of C̄ with the Gilman color test for RMgX compounds see (568).]

[For study of relative reactivity of C̄ as compared with various other organic compounds in competition for C_6H_5MgBr see (569).]

Behavior of C̄ with other miscellaneous organometallic compounds. This topic cannot be treated extensively, but the following examples, mainly from the recent literature, will serve as lead references.

[C̄ with C_6H_5Li gives (570) no benzophenone and only 42% yield triphenylcarbinol (1:5985). — C̄ with Na phenylacetylene (571) (572) or Ag phenylacetylene (572) gives (74% yield (571)) phenyl phenylethynyl ketone (benzoyl-phenylacetylene) [Beil. VII-498, VII_1-(275)].]

[C̄ + EtCu (573) in ether gives (22% yield (573)) ethyl phenyl ketone (propiophenone) (1:5525). — C̄ with C_6H_5Cu (573) in ether gives (55% yield (573)) benzophenone (1:5150).]

[C̄ + Et_2Hg gives (small yield (574)) propiophenone (1:5525). — C̄ with $(C_6H_5)_2Hg$ in C_6H_6 gives (575) benzophenone (1:5150). — C̄ with excess di-p-tolyl mercury in CCl_4 fails (576) to react.]

[C̄ with Me_2Be gives (577) dimethyl-phenyl-carbinol [Beil. VI-506, VI_2-(477)]. — C̄ with Me_2Cd gives (85% yield (578)) methyl phenyl ketone (acetophenone) (1:5515). — C̄ with Et_2Cd gives (50% yield (578)) ethyl phenyl ketone (propiophenone) (1:5525). — C̄ with $(C_6H_5)_2Cd$ gives (57% yield (578)) diphenyl ketone (bezophenone) (1:5150). — C̄ with Me_2Zn gives (579) methyl phenyl ketone (acetophenone) (1:5515). — C̄ with Et_2Zn (580) (581) or with EtZnI (582) gives ethyl phenyl ketone (propiophenone) (1:5525).]

Ⓓ Benzamide: cryst. from hot aq., m.p. 130°. [For methods of prepn. see above text under behavior of C̄ with various inorganic nitrogen compounds.]

Ⓓ Benzanilide: lfts. from alc., m.p. 160°. [From C̄ with aniline directly (583), in ether contg. dry K_2CO_3 (584), in C_6H_6 (585), in toluene (586), in pyridine (or other tertiary amines) (587), in dil. aq. HCl (588), in AcOH/aq. NaOAc (589), or aq. NaOH. — For study of rate of reaction of C̄ with aniline in aq. at various temperatures 0–60° (590),

in C_6H_6 at 25° (591) cf. (585), in hexane at 25° (592), or in CCl_4 at 25° (592) see indic. refs. — Note that C̄ with aniline hydrochloride in boilg. C_6H_6 gives almost quant yield (530) benzanilide.]

Ⓓ **Benz-o-toluidide:** ndls. from AcOEt/acetone, m.p. 145–146° (594) (595), 144.3–144 6° cor. (586), 142–143° (593), 142° (587). [From C̄ with o-toluidine (593) (594) in pres. of dil. (4%) aq. NaOH (595), or in pyridine (or other tertiary bases) (75% yield (587)), or in boilg. toluene (586).]

Ⓓ *Benz-m-toluidide: cryst. from dil alc, m.p. 126° (587), 124.3–124.7° cor. (586), 125°* (596). [From C̄ with m-toluidine (596) in pyridine (or other tertiary bases) (80% yield (587)) or in boilg toluene (586).]

Ⓓ **Benz-p-toluidide:** ndls. from alc., m.p. 158° (597), 157.7–158.2° cor. (586), 157° (587). [From C̄ with p-toluidine (598) (599) in pyridine (or other tertiary bases) (85% yield (587)) or in boilg. toluene (586).]

Ⓓ **Benz-α-naphthalide:** ndls from alc. or AcOH, m.p. 161–162° (600), 159–160° (601) cor. (608), 159° (587), 156° (602), 155–156° (603). [From C̄ with α-naphthylamine (604) (602) in aq. NaOH (603), pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/aq. NaOAc (589). — For mol. cpd. of benz-α-naphthalide with 1,3,5-trinitrobenzene, viz., $\bar{C}'.C_6H_3(NO_2)_3$, yel. ndls from alc. soln. of components, m.p. 131–132° (605); see indic. refs. — For behavior of C̄ with α-naphthylamine in pres. of $ZnCl_2$ at 175–180° yielding 1-benzoylamino-4-benzoylnaphthalene, m.p. 178°, 1-benzoylamino-2,4-dibenzoylnaphthalene, m p. 224–226°, etc., see (606) (607).]

Ⓓ **Benz-β-naphthalide:** ndls. from C_6H_6 or AcOH, m.p. 162–163° (609), 162° (587), 161° (612), 157° (610), 156.5–157° cor. (608). [From C̄ with β-naphthylamine (611) (610) in ether + K_2CO_3 (612), in pyridine (or other tertiary bases) (80% yield (587)), or in AcOH/aq. NaOAc (589).]

Ⓓ **Benzhydrazide:** m p. *112°*. [See above text under behavior of C̄ with various inorganic nitrogen compounds, specifically with $NH_2.NH_2$.]

Ⓓ **β-Benzoylphenylhydrazine** (N-Anilinobenzhydrazide). pr. from alc., m.p. 168°. [See above text under behavior of C̄ with organic nitrogen compounds, specifically with arylhydrazines]

—— **β-Benzoyl-p-nitrophenylhydrazine** (N-(p-nitroanilino)benzhydrazide): ndls. from alc., m.p. 193°. See above text under behavior of C̄ with organic nitrogen compounds, specifically with arylhydrazines.

Ⓓ **β-Benzoyl-2,4-dinitrophenylhydrazine** (N-(2,4-dinitroanilino)benzhydrazide): or.-red lfts. from alc , m.p. 206–207°. [See above text under behavior of C̄ with organic nitrogen compounds, specifically with arylhydrazines.]

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(501) Raiford, Lankelma, *J. Am. Chem. Soc.* **47**, 1111–1123 (1925) (502) Raiford, Colbert, *J. Am. Chem. Soc.* **47**, 1454–1458 (1925). (503) Raiford, Clark, *J. Am. Chem. Soc.* **48**, 483–489 (1926). (504) Raiford, Talbot, *J. Am. Chem. Soc.* **49**, 559–561 (1927) (505) Raiford, Mortenson, *J. Am. Chem. Soc.* **50**, 1201–1204 (1928) (506) Raiford, Grosz, *J. Am. Chem. Soc.* **53**, 3420–3426 (1931). (507) Raiford, Inman, *J. Am. Chem. Soc.* **56**, 1586–1590 (1934). (508) Raiford, Shelton, *J. Org. Chem.* **4**, 207–219 (1939) (509) Raiford, Alexander, *J. Org. Chem.* **5**, 300–312 (1940). (510) Bacher, Raiford, *Proc. Iowa Acad. Sci.* **50**, 247–251 (1943). *C.A.* **38**, 2327 (1944).

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(541) von Braun, *Ber.* **36**, 3524, Note (1903) (542) von Braun, *Ber.* **37**, 3210–3213 (1904). (543) von Braun, Steindorff, *Ber.* **38**, 2336–2339 (1905). (544) Merck, Ger. 164,365, Oct. 28,

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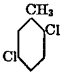
(601) Hofmann, *Ber.* **20**, 1798 (1887). (602) Hübner, Ebell, *Ann.* **208**, 334 (1881). (603) Berlingozzi, Barni, *Gazz. chim. ital.* **50**, I 219 (1920). (604) Church, *Chem. News* **5**, 324 (1862). [illegible] 6) Dziewonski, Sternbach, [illegible] *Cent.* **1934**, II 1621]; *C.A.* [illegible] -2592; not in *C.A.* (607) [illegible] *th. nat.* **1935-A**, 327–332; *Cent.* **1936**, I 2093; *C.A.* **30**, 2971 (1936). (608) Loevenich, Loeser, *Ber.* **60**, 322–323 (1927). (609) Young, Clark, *J. Chem. Soc.* **71**, 1203 (1897). (610) Klopsch, *Ber.* **18**, 1585 (1885).

(611) Cosiner, *Ber.* **14**, 59 (1881). (612) Ley, *Ber.* **34**, 2629–2630 (1901).

3:6245 2,5-DICHLOROTOLUENE



$C_7H_6Cl_2$

Beil. V - 296
V_1—
V_2-(231)

B.P.		M.P.		
200°	at 770 mm. (1)	5°	(2) (3)	$D^{20}_{20} = 1.2535$ (6)
199°	at 761 mm. (2)	4–5°	(6)	
198–200°	at 760 mm. (3)			
197.7–198.1°	at 760 mm. (4)			
196–198°	at 756 mm. (5)			
194°	at 745 mm. (6)			
82.5–82.8°	at 15 mm. (4)			

[For prepn. of $\bar{C}$ from 5-chloro-2-aminotoluene [Beil. XII-835] via diazotization and use of Cu_2Cl_2 reaction (yield: 87.6% (1), 70% (3) (7)) (4) (6) (2) see indic. refs.; from K (1) or Na (5) salt of 2,5-dichlorotoluenesulfonic acid-6 by hydrolysis in conc. H_2SO_4 with superheated steam see (1) (5); for formn. of $\bar{C}$ (together with other isomers) from toluene with Cl_2 in pres. of $FeCl_3$ or $MoCl_5$ see (8), from *o*-chlorotoluene (3:8245) or *m*-chlorotoluene (3:8275) with Cl_2 in pres. of Al/Hg see (9).]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg yields (10) both 2,3,6-trichlorotoluene (3:0625) and 2,4,5-trichlorotoluene (3:2100).]

$\bar{C}$ on mononitration in cold with mixt. of 1½ pts. conc. HNO_3 ($D = 1.4$) and 3 pts. conc. H_2SO_4 yields (3) (11) 2,5-dichloro-4-nitrotoluene [Beil. V-332], ndls. from alc. + ether, m.p. 50–51° (3); $\bar{C}$ on dinitration with mixt. of 7 pts. fumg. HNO_3 ($D = 1.5$) and 3½ pts. conc. H_2SO_4 at 100° yields (3) (11) 2,5-dichloro-4,6-dinitrotoluene [Beil. V-345], cryst. from AcOH, m.p. 100–101° (3).

$\bar{C}$ on oxidn. with dil. HNO_3 in s.t. at 120–150° gives (yield: 82% (7), 60% (2)) (3) (5) (6) 2,5-dichlorobenzoic acid (3:4340), m.p. 154°.

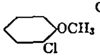
$\bar{C}$ on sulfonation with fumg. H_2SO_4 yields (1) (3) (12) 2,5-dichlorotoluenesulfonic acid-4 (corresp. sulfonyl chloride, m.p. 43° (1) (12), corresp. sulfonamide, m.p. 191–192° (1) (3) (12)).

[For behavior of $\bar{C}$ with NaOMe see (2).]

3:6245 (1) Wynne, *J. Chem. Soc.* **61**, 1049–1053 (1892). (2) de Crauw, *Rec. trav. chim.* **50**, 773, 783, 788 (1931) (3) Cohen, Dakin, *J. Chem. Soc.* **79**, 1130–1131 (1901). (4) Kohlrausch, Stockmair, Ypsilanti, *Monatsh.* **67**, 90 (1935) (5) Turner, Wynne, *J. Chem. Soc.* **1936**, 712. (6) Lellmann, Klotz, *Ann.* **231**, 318–319 (1885) (7) Feldman, Kopeliowitsch, *Arch. Pharm.* **273**, 491 (1935). (8) Wynne, *Proc. Chem. Soc.* **17**, 116 (1901). (9) Ref 3, pp. 1117–1118. (10) Cohen, Dakin, *J. Chem. Soc.* **81**, 1342 (1902).
(11) Cohen, Dakin, *J. Chem. Soc.* **81**, 1347 (1902). (12) Silvester, Wynne, *J. Chem. Soc.* **1936**, 692.

3:6255 *o*-CHLOROANISOLE C_7H_7OCl Beil. VI - 184

(*o*-Chlorophenyl methyl ether) VI$_1$-(99) VI$_2$-(171)



B.P.		
198.5–199.5°		(1)
195–196°		(2)
194–200° u.c.	at 751 mm.	(3)
92–93°	at 20 mm.	(18)
90–91°	at 16 mm.	(4)
100°	at 13 mm.	(5)
80.5–81.4°	at 10 mm.	(1)

$D_4^{25} = 1.1865$ (18) $n_D^{25} = 1.5433$ (18)
$D_4^{12.6} = 1.1978$ (6) $n_{He}^{12.6} = 1.54786$ (6)

Oil with odor like acetophenone (7). — Volatile with steam.

[For prepn. of $\bar{C}$ from *o*-chlorophenol (3:5980) by methylation with Me_2SO_4 + KOH (3) or with MeI + KOH in MeOH in s.t. at 130° (8) see (3) (8); from *o*-aminoanisole via diazo and Sandmeyer reactns. see (9) (2); from guaiacol (1:1405) with PCl_5 see (8); from *o*-nitroanisole with $SOCl_2$ at 180–200° see (10).]

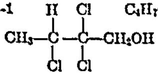
$\bar{C}$ on mononitration with fumg. HNO_3 (8) (11) (12) or with HNO_3 ($D = 1.5$) in Ac_2O (5) yields a mixt. of all 4 possible mononitro products from which the 3-nitro- and 5-nitro isomers are removed by refluxing with 5% NaOH for 1 hr. (5); the unaffected residue extracted by ether consists of 2-chloro-4-nitroanisole, m.p. 94° (5), and 2-chloro-6-nitroanisole, m.p. 53° (5); for f.p./compn. data on this system see (5). [2-Chloro-4,6-dinitroanisole [Beil. VI-260] has m.p. 36° (16), 37° (17).]

[For a study of the reactn. kinetics of the splitting of $\bar{C}$ in acid soln. see (15).]

Ⓓ 3-Chloro-4-methoxybenzenesulfonamide: cryst. from dil. alc., m.p. 130–131° u.c. (13), 130° cor. (14). [From Č + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p. 77–80° (14), to sulfonamide with $(NH_4)_2CO_3$; 85% yield (13).] [A by-product, 3,3′-dichloro-4,4′-dimethoxydiphenyl sulfone, m.p. 165–166° cor. (14) (but unlike the sulfonamide insol. in alk.), has also been observed (14).]

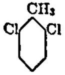
3:6255 (1) Reitz, Ypsilanti, *Monatsh.* **66**, 304 (1935). (2) Gattermann, *J. prakt. Chem.* (2) **59**, 583 (1899). (3) Kohn, Sussmann, *Monatsh.* **48**, 196–197 (1927). (4) Hayashi, *J. prakt. Chem.* (2) **123**, 293 (1929). (5) Ingold, Smith, *J. Chem. Soc.* **1927**, 1690–1695. (6) von Auwers, *Z. physik. Chem.* **A-158**, 418 (1932). (7) Holleman, *Rec. trav. chim.* **37**, 104 (1918). (8) Fischli, *Ber.* **11**, 1463 (1878). (9) Wallach, Heusler, *Ann.* **243**, 237–238 (1888). (10) Meyer, *Monatsh.* **36**, 728 (1915).

(11) Reverdin, *Ber.* **29**, 2598 (1896). (12) Reverdin, Eckhard, *Ber.* **32**, 2622 (1899). (13) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603–604 (1940). (14) Child, *J. Chem. Soc.* **1932**, 718. (15) Ghaswalla, Donnan, *J. Chem. Soc.* **1936**, 1341–1346. (16) Schouten, *Rec. trav. chim.* **56**, 550 (1937). (17) van de Vliet, *Rec. trav. chim.* **43**, 623–624 (1924). (18) Anzillotti, Curran, *J. Am. Chem. Soc.* **65**, 609 (1943).

—— *d,l*-2,2,3-TRICHLOROBUTANOL-1  $C_4H_7OCl_3$ Beil. I - 369 I_1— I_2-(398)

B.P. 199–200° **M.P. 62°**

See 3:1336. *Division A: Solids.*

3:6270 2,6-DICHLOROTOLUENE  $C_7H_6Cl_2$ Beil. V - 296 V_1— V_2-(231)

B.P.
199–200° at 760 mm. (13) (1)
198–200° (2)
198° at 760 mm. (3)
197–199° at 757 mm. (4)
54–56° at 8 mm. (5)

D_4^{20} = **1.2686** (5) n_D^{20} = **1.5510** (5)

[For prepn. of Č from 6-chloro-2-aminotoluene [Beil. XII-836, XII_1-(389)] via diazotization and use of Cu_2Cl_2 reactn. (70% yield (2)) (1) (3) see indic. refs.; from 2,6-dichlorotoluenesulfonic acid-4 (itself obtd. by chlorination of *p*-toluenesulfonyl chloride and subsequent hydrolysis) by hydrolysis in conc. H_2SO_4 with superheated steam (yield 42–50% (5)) (4) (6) together with 2,3,6-trichlorotoluene (3:0625) as by-product (5) (6) see indic. refs.; for formn. of Č (together with other isomers) from toluene with Cl_2 in pres. of $MoCl_5$ (7) (8) (9), from *o*-chlorotoluene (3:8245) with Cl_2 in pres. of Fe (9) or Al/Hg (10), or from 2,6-dichlorobenzaldehyde hydrazone by Wolff-Kishner reduction (32–80% yield (19)) see indic. refs.]

[Č with Cl_2 in pres. of Al/Hg yields (11) 2,3,6-trichlorotoluene (3:0625); Č at its b.p. in u.v. light treated with Cl_2 yields (5) 2,6-dichlorobenzyl chloride (3:0410) cryst. from lgr. or ether, m.p. 39–40° (5).]

[Č with Br_2 at 170° in sunlight (2) yields (2) (12) 2,6-dichlorobenzyl bromide which on oxidn. with alk. $KMnO_4$ yields (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p. 143–144°.]

$\bar{C}$ on mononitration in cold with 2 pts. fumg. HNO_3 (11) or with mixt. of 2 pts. conc. HNO_3 (D = 1.4) + 3 pts. conc. H_2SO_4 at 100° (3) yields 2,6-dichloro-3-nitrotoluene [Beil. V-332], ndls. from alc. + AcOH, m p. 53° (3), 52–53° (11), 50° (13); note that the other possible isomer, viz., 2,6-dichloro-4-nitrotoluene, m.p. 65° (14), 63–64° (15), has been obtd. only by other means. — $\bar{C}$ on dinitration with mixt. of 7 pts. fumg. HNO_3 (D = 1.5) and 3½ pts. conc. H_2SO_4 at 100° yields (3) 2,6-dichloro-3,5-dinitrotoluene [Beil. V-345], ndls. from alc., m.p. 121–122° (3), 121° (4) (14); note that the isomeric 2,6-dichloro-3,4-dinitrotoluene, m.p. 130–131° (14), 129–130° (16), has been obtd. only by other means.

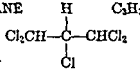
$\bar{C}$ is extremely resistant to oxidn. either with dil. HNO_3 (9) (1) (3), aq. alk. $KMnO_4$ (4) (12), acid $KMnO_4$ (12), $KMnO_4$ in acetone (4), CrO_3 in H_2SO_4 or AcOH (12), or $K_2Cr_2O_7$ in H_2SO_4 (12); by conversion of $\bar{C}$ with Br_2 to 2,6-dichlorobenzyl bromide (see above) and oxidn. of this with alk. $KMnO_4$ (2) (12) 2,6-dichlorobenzoic acid (3:4200), m.p. 143–144°, is obtd. in 57% yield (12).

$\bar{C}$ on sulfonation with fumg. H_2SO_4 (3) yields 2,6-dichlorotoluenesulfonic acid-3 (corresp. sulfonyl chloride, m.p. 60° (3) (13), corresp. sulfonamide, m.p. 204° (3) (13), 199–201° u.c. (17)); $\bar{C}$ on treatment with chlorosulfonic acid in $CHCl_3$ as directed (17) cf. (18) yields 2,6-dichlorotoluenesulfonyl chloride-3, m.p. 54–56° u.c. (17), 60° (3) (13) (18).

3:6270 (1) Wynne, Greeves, *Proc. Chem. Soc.* **11**, 151–152 (1895). (2) Lehmstedt, Schrader, *Ber.* **70**, 1530 (1937). (3) Cohen, Dakin, *J. Chem. Soc.* **79**, 1131–1133 (1901). (4) Davies, *J. Chem. Soc.* **119**, 873 (1921). (5) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 657–659 (1932). (6) Geigy and Co., Ger. 210,856, June 16, 1909; *Cent.* **1909**, II 79–80. (7) Aronheim, Dietrich, *Ber.* **8**, 1402 (1875). (8) Schultz, *Ann.* **187**, 263 (1877). (9) Claus, Stavenhagen, *Ann.* **269**, 231 (1892). (10) Ref. 3, p. 1117.

(11) Cohen, Dakin, *J. Chem. Soc.* **81**, 1343, 1346 (1902). (12) Norris, Bearse, *J. Am. Chem. Soc.* **62**, 956 (1940). (13) Silvester, Wynne, *J. Chem. Soc.* **1936**, 692, 695. (14) Davies, *J. Chem. Soc.* **121**, 812, 814 (1922). (15) Levy, Stephen, *J. Chem. Soc.* **1931**, 78–79. (16) Davies, Leeper, *J. Chem. Soc.* **1926**, 1416. (17) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 512–513 (1940). (18) I.G., Brit. 281,290, Jan. 25, 1928; French 644,319, Oct. 5, 1928; *Cent.* **1929**, II 352. (19) Lock, Stach, *Ber.* **76**, 1252–1256 (1943).

3:6280 1,1,2,3,3-PENTACHLOROPROPANE (*sym.*-Pentachloropropane)



$C_3H_3Cl_5$

Beil. I — I_1-(34) I_2—

B.P.

198–200° (1)
126° at 90 mm. (1)
98–100° at 20 mm. (2)

D_4^{34} = **1.6086** (1)

$n_D^{15.5}$ = **1.5131** (1)

Colorless liq. — Dissolves sulfur and vulcanized rubber.

[For prepn. (yields: 70–75% (3), 63% (2), 46% at 17° for 22 hrs. (3)) from $CHCl_3$ (3:5050) + *sym.*-dichloroethylene (3:5030) + $AlCl_3$ by stirring with sand for 20 hrs. at 30° see (2) (3) (4).]

$\bar{C}$ with alc. KOH (1 mole) gives (70% yield (2)) 1,2,3,3-tetrachloropropene-1 (3:5920), b.p. 165–167° (2).

3:6280 (1) Prins, *J. prakt. Chem.* (2) **89**, 421 (1914). (2) Heilbron, Heslop, Irving, *J. Chem. Soc.* **1936**, 782–783. (3) Prins, Engelhard, *Rec. trav. chim.* **54**, 307–312 (1935). (4) Prins, Ger. 261,689, July 2, 1913, *Cent.* **1913**, II 394; [*C.A.* **7**, 3641 (1913)].

3:6290 2,4-DICHLOROTOLUENE  $C_7H_6Cl_2$ Beil. V - 295 V_1-(152) V_2-(230)

B.P.		F.P.	
199.9–200.5° cor. at 760 mm.	(1)	−13.5° (1)	D^{20}_{20} = 1.2498 (1)
198–200°	(2)		1.24597 (6)
196.4–198.2°	(3)		
196–197.5°	(4)		n^{22}_D = 1.5480 (1)
196–197.0°	(5)		
194° u.c. at 745 mm.	(6)		
82.0–82.9° at 15 mm.	(3)		

For f.p./compn. diagram of system: C̄ + 3,4-dichlorotoluene (3:6355) see (1); the eutectic conts. 48% C̄ and freezes about −38° (1).

[For prepn. of C̄ from 2-chloro-4-aminotoluene [Beil. XII-988, XII_1-(435)] via diazotization and use of Cu_2Cl_2 reaction (yield: 72% (5), 30% (6)) see indic. refs.; similarly from 4-chloro-2-aminotoluene [Beil. XII-835, XII_1-(389)] see (2); from 2,4-diaminotoluene [Beil. XIII-124, $XIII_1$-(40)] via tetrazotization and use of $CuCl_2$ reaction (yield: 75% (7), 57% (16), 45% (4)) (3) see indic. refs.; from toluene + $AlCl_3$ + SO_2Cl_2 at 70° (68% yield) see (10).]

[For formn. of C̄ (58% together with 42% 3,4-dichlorotoluene (3:6355) from p-chlorotoluene (3:8287) with Cl_2 in pres. of Fe see (1); for formn. of C̄ (together with other isomers) from toluene with Cl_2 in pres. of $FeCl_3$ or $MoCl_5$ (8) or by electrolysis in conc. HCl/AcOH soln. (9) see indic. refs.; from o-chlorotoluene (3:8245) or p-chlorotoluene (3:8287) with Cl_2 in pres. of $FeCl_3$ or $MoCl_5$ (8) or Al/Hg (11) see indic. refs.; from potassium salt of 2,4-dichlorotoluenesulfonic acid-5 (12), sodium salt of 2,4-dichlorotoluenesulfonic acid-6 (12), or the sodium salt or amide of 2,4-dichlorotoluenesulfonic acid-3 (12) by hydrolysis in H_3PO_4 with steam at 240° see indic. refs.]

[C̄ with Cl_2 in pres. of Fe (13) or of Al/Hg (14) yields 2,4,5-trichlorotoluene (3:2100) together with other isomers; C̄ with Br_2 at 180–200° yields (15) 2,4-dichlorobenzal dibromide which upon hydrolysis with conc. H_2SO_4 as directed gives 92% overall yield 2,4-dichlorobenzaldehyde (3:1800), m.p. 74.5° (15) (for similar reaction with Cl_2 see (5)).]

[C̄ with $AlCl_3$ + phthalic anhydride gives (60% yield (16)) (17) o-(2,4-dichloro-5-methyl)benzoyl-benzoic acid, cryst. from hot toluene, m.p. 140° (16); this prod. htd. 2 hrs. at 100° with 20 pts. conc. H_2SO_4 + 0.2 pt. H_3BO_3 ring-closes yielding 2,4-dichloro-1-methylanthraquinone, yel. cryst. from $CHCl_3$, m.p. 155° (16).]

C̄ on mononitration, e.g., with cold mixt. of 2 pts. conc. HNO_3 (D = 1.42) + 3 pts. conc. H_2SO_4 (2), yields (2) (8) 2,4-dichloro-5-nitrotoluene [Beil. V-332, V_1-(163)], long hard ndls. from alc., m.p. 54–55° (2), 55° (18), 53° (8), 49–50° (19); C̄ on dinitration, e.g., with 7 pts. fumg. HNO_3 (D = 1.5) + 3½ pts. conc. H_2SO_4 (2), yields (2) (8) (10) 2,4-dichloro-3,5-dinitrotoluene [Beil. V-345, V_1-(169)], ndls. from MeOH, m.p. 104° (2) (18) (10)

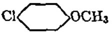
C̄ on oxidn. with dil. HNO_3 in s t. at 130–150° (2) (6) (12), with alk. $KMnO_4$ (70% yield (25)), with $Na_2Cr_2O_7$ + H_2SO_4 (60% yield (20)), or on electrolytic oxidn. (6.5% yield (21)) gives 2,4-dichlorobenzoic acid (3:4560), m.p. 164°.

C̄ on sulfonation with fumg. H_2SO_4 yields (2) (22) 2,4-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 72° (22), 71° (2) (24), corresp. sulfonamide, m.p. 176° (2) (22); 175–176° u c. (23)); C̄ on treatment with chlorosulfonic acid in $CHCl_3$ as directed (23) cf. (24) yields 2,4-dichlorotoluenesulfonyl chloride, m.p. 71–72° u.c. (23), 71° (24).

3:6290 (1) ... 4, 344–349 (1937). (2) Cohen, Da... Stockmair, Ypsilanti, *Monatsh.* **67** ... *chim.* **51**, 103, 109 (1932). (6) I... *J. Chem. Soc.* **1935**, 530. (8) S... stein, *Ber.* **49**, 2181–2487 (1916...

(11) Ref. 2, pp. 1116–1117. ... Kopehowitsch, *Arch. Pharm.* **273**, 493–495 (1935) (14) Cohen, Dakin, *J. Chem. Soc.* **81**, 1340–1341 (1902). (15) Lock, Bock, *Ber.* **70**, 923 (1937). (16) Stouder, Adams, *J. Am. Chem. Soc.* **49**, 2044–2045 (1927). (17) Adams (to Newport Co), U.S. 1,711,165, Apr 30, 1929; *Cent.* **1929**, II 796; *C.A.* **23**, 2989 (1929). (18) Blanksma, *Rec trav chim* **29**, 415 (1910). (19) Dadswell, Kenner, *J. Chem Soc* **1927**, 585. (20) Magidsson, Grigorowski, Russ. 47,689, July 31, 1936, *Cent.* **1937**, I 430–431.

(21) Fichter, Adler, *Helv. Chim. Acta* **9**, 286 (1926). (22) Silvester, Wynne, *J. Chem Soc.* **1936**, 692 (23) Huntress, Carten, *J. Am. Chem Soc.* **62**, 512–513 (1940). (24) I.G., Brit. 281,290, Jan. 25, 1928; French 644,319, Oct 5, 1928; *Cent.* **1929**, II 352. (25) Bornwater, Holleman, *Rec trav. chim.* **31**, 226–230 (1912).

3:6300 *p*-CHLOROANISOLE (*p*-Chlorophenyl methyl ether)  C_7H_7OCl Beil. VI - 186 VI_1-(101) V_2-(175)

B.P.			B.P. *Cont.*				
200°		(1) (2) (13)	**193–197° u.c.**		(7)	$D_4^{12.8}$ = **1.1851**	(11)
198–200°		(3)	**94–96°**	at 25 mm.	(8)		
197.5°	at 760 mm.	(20)	**88°**	at 18 mm.	(9)		
197.7°	at 759 mm.	(4)	**79.5°**	at 12 mm.	(10)	$n_{He}^{12.8}$ = **1.54015**	(11)
196.6–197°	at 759 mm.	(5)	**74.8–75.4°**	at 10 mm.	(5)		
194–198° u.c.		(6)					

Insol. aq.; eas. sol. alc., ether, $CHCl_3$. — Does not freeze at −18° (3).

[For prepn. from *p*-chlorophenol (3:0475) by methylation with Me_2SO_4 + alk. (7) (6) (1) (60% yield (10)) or with MeI + KOH in s.t. at 120–140° (3) see indic. refs.; from anisole (1:7445) + PCl_5 (2) (100% yield (12)) or SO_2Cl_2 (4) see indic. refs.; from *p*-chloroaniline by diazotization and htg. with MeOH see (13).]

C̄ on mononitration as directed (7) (14) (6) gives (93% yield (6)) 4-chloro-2-nitroanisole [Beil VI-240], pale yel. lfts. from pet. eth., ndls. or pr. from alc., m.p. 98.5° (15), 98° (14), 96–97.5° (6), 96° (7). [The principal dinitration product, 4-chloro-2,6-dinitroanisole [Beil. VI-260] (best prepd. (16) by further nitration of the 2-nitro prod.), has m.p. 66° (16), 65° (17), 64° (18).]

C̄ on htg. with conc. HCl in s.t. (12) or with NaOMe in MeOH in s.t. at 176° (21) gives MeCl (3:7005) + *p*-chlorophenol (3:0475). [For study of rate of splitting by acids see (19).]

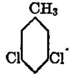
Ⓓ **5-Chloro-2-methoxybenzenesulfonamide:** m.p. 154° (22), 150–151° (23). [From C̄ + chlorosulfonic acid followed by conversion of the resultant sulfonyl chloride, m.p. 104° (22), to sulfonamide with $(NH_4)_2CO_3$; 82% yield (23).]

3:6300 (1) von Auwers, Baum, Lorenz, *J. prakt Chem* (2) **115**, 89 (1927). (2) Henry, *Ber.* **2**, 710 (1869) (3) Beilstein, Kurbatow, *Ann.* **176**, 30 (1875) (4) Peratoner, Ortoleva, *Gazz chim ital.* **28**, I 226 (1898) (5) Reitz, Ypsilanti, *Monatsh.* **66**, 305 (1935) (6) Ingold, Smith, Vass, *J. Chem. Soc.* **1927**, 1248 (7) Kohn, Kramer, *Monatsh* **49**, 151 (1928). (8) Hayashi, *J. prakt. Chem.* (2) **123**, 297 (1929). (9) Jones, *J Chem. Soc.* **1942**, 419. (10) Bergmann, Engel, *Z physik Chem* **B-15**, 95–96 (1931).

(11) von Auwers, *Z physik. Chem.* **A-158**, 418 (1932). (12) Autenrieth, *Arch. Pharm* **233**, 31–32 (1895). (13) Cameron, *Am. Chem. J.* **20**, 241 (1898). (14) Reverdin, Eckhard, *Ber.* **32**, 2623 (1899). (15) Reverdin, *Ber.* **29**, 2599 (1896). (16) Schouten, *Rec. trav. chim.* **56**, 555 (1937).

(17) van de Vliet, *Rec. trav. chim.* **43**, 622 (1924). (18) Ref. 7, pp. 154–155. (19) Ghaswalla, Donnan, *J. Chem. Soc.* **1936**, 1341–1346. (20) Paulsen, *Monatsh.* **72**, 257 (1939).
(21) de Lange, *Rec. trav. chim.* **38**, 103 (1918). (22) Gauntlett, Smiles, *J. Chem. Soc.* **127**, 2745 (1925). (23) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 603–604 (1940).

3:6310 3,5-DICHLOROTOLUENE $C_7H_6Cl_2$ Beil. V-296
V_1—
V_2—



B.P.			M.P.		
201–202° cor.	at 760 mm.	(1)	26–27°	(10)	n_D^{20} = 1.5438 (12)
200°	at 750 mm.	(2)	26°	(2) (3) (5) (6) (7)	
195°	at 729 mm.	(3)	24.8–25.0°	(4)	
78–79°	at 9 mm.	(12)	24.5°	(12)	

Sublimes at ord. temp. (3).

[For prepn. of $\bar{C}$ from 3,5-dichloro-2-aminotoluene [Beil. XII-837] via diazotization and reactn. with alc. (yield: 80–85% (2), 57% (5)) (1) see indic. refs.; similarly from 3,5-dichloro-4-aminotoluene [Beil. XII-990] see (3) (4); for formn. of $\bar{C}$ from 3,5-dibromo-2-aminotoluene [Beil. XII-840, XII_1-(390)] or from 3,5-dibromo-4-aminotoluene [Beil. XII-993, XII_1-(437)] by diazotization followed by treatment with HCl gas in alc. see (6); for prepn. from 3,5-dichloro-2-acetaminotoluene by hydrolysis with EtOH/HCl followed by HNO_2 (34% yield) see (12).]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg gives (7) exclusively 2,3,5-trichlorotoluene (3:0610), m.p. 43–45° (7); $\bar{C}$ with Cl_2 at 180–190° for 10–12 hrs. gives (2) 3,5-dichlorobenzal dichloride (3:0370).]

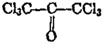
[$\bar{C}$ with Br_2 in pres. of Fe gives in cold (70% yield (8)) 2-bromo-3,5-dichlorotoluene, ndls. from alc., m.p. 33.5° (8).]

$\bar{C}$ on mononitration by soln. in ice-cold fumg. HNO_3 (D = 1.52) (9) yields 3,5-dichloro-2-nitrotoluene [Beil. V-331], ndls. from alc. + AcOH, m.p. 61–62° (5) (crude prod. m.p. 57° (9)); $\bar{C}$ on dinitration with mixt. of 4 pts. HNO_3 (D = 1.5) + 4 pts. conc. H_2SO_4 (5) or the above mononitro deriv. on further nitration with HNO_3 (D = 1.52) at 65° (9) yields 3,5-dichloro-2,6-dinitrotoluene, ndls. from alc., m.p. 99–100° (5); note that the crude dinitration prod. often melts about 90° (9), probably because of contamination with 3,5-dichloro-2,4-dinitrotoluene, m.p. 127° (9).

$\bar{C}$ on oxidn. with dil. HNO_3 (5) (10) in s.t. at 170° (3) yields 3,5-dichlorobenzoic acid (3:4840), m.p. 188°.

$\bar{C}$ on sulfonation with fumg. H_2SO_4 yields (5) (11) 3,5-dichlorotoluenesulfonic acid-2, (corresp. sulfonyl chloride, m.p. 44–45° (5) (11), corresp. sulfonamide, m.p. 168–169° (5) (11)).

3:6310 (1) Wynne, Greeves, *Proc. Chem. Soc.* **11**, 151–152 (1895). (2) Asinger, Lock, *Monatsh.* **62**, 345 (1933). (3) Lellmann, Klotz, *Ann.* **231**, 323–324 (1885). (4) Maryott, Hobbs, Gross, *J. Am. Chem. Soc.* **62**, 2321 (1940). (5) Cohen, Dakin, *J. Chem. Soc.* **79**, 1133–1134 (1901). (6) Hantzsch, *Ber.* **30**, 2344–2346 (1897). (7) Cohen, Dakin, *J. Chem. Soc.* **81**, 1343–1344 (1902). (8) [illegible] **139**, [illegible] (9) Borsche, Trautner, *Ann.* **447**, 13 (1926). (1[illegible] (12) Marvel, Overberger, Allen, Johnston, Sa[illegible]

3:6312 HEXACHLOROPROPANONE-2  C_3OCl_6 Beil. I - 657
(Hexachloroacetone) I_1— I_2—

B.P.		F.P.		
202–204°	(1) (7)	−2°	(1)	D_{12}^{12} = 1.744 (1) (7)
110° at 40 mm.	(2)	−3 to −4°	(2)	

[*See also pentachloropropanone-2* (3:6205).]

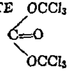
Colorless limpid liq. with odor which although faint at low temp. becomes sharp and lachrymatory at higher temps. — $\bar{C}$ is spar. sol. aq. but with it forms a cryst. monohydrate, m.p. + 15°, alm. insol. aq.

[For prepn. of $\bar{C}$ from acetone (1:5400) in 90% AcOH + a little HCl with Cl_2 for 12 hrs. at room temp., followed (after addn of NaOAc) by 40 hrs. further chlorination at b.p. (2), or with Cl_2 in sunlight (1) (some pentachloroacetone (3:6205) is formed by either method): for prepn. of $\bar{C}$ from chloracetone (3:5425) with Cl_2 at 50–100° in light (3) (4) or under press. (5) see indic. refs.; for formn. of $\bar{C}$ from citric acid (1:0455) in conc. aq. soln. with Cl_2 in sunlight (1) (6) (7), or from glycerol (1:6540) with Cl_2 in pres. of I_2 (7), see indic. refs.]

$\bar{C}$ on stdg. with aq. at 30° (2) or with aq. in s.t. at 120° (1) readily undergoes hydrolytic cleavage yielding chloroform (3:5050) and trichloroacetic acid (3:1150).

$\bar{C}$ with conc. aq. NH_4OH readily splits yielding (1) chloroform (3:5050) and trichloroacetamide, spar. sol. aq., m.p. 141°; similarly $\bar{C}$ with aniline yields (1) chloroform (3:5050) and trichloroacetanilide, m p. 95–97°.

3:6312 (1) Cloëz, *Ann. chim.* (6) **9**, 199–205 (1886) (2) Edwards, Evans, Wilson, *J. Chem. Soc.* **1937**, 1944–1945. (3) Heisel, Hendschel (to I.G.), U.S 2,199,934, May 7, 1940; *C.A.* **34**, 5855 (1940). (4) I.G., French 816,956, Aug 21, 1937, *Cent.* **1938**, I 2216. (5) I G, French 837,741, Feb. 20, 1939; *Cent.* **1939**, II 228. (6) Städeler, *Ann* **111**, 299–300 (1859). (7) Cloëz, *Ann.* **122**, 119–122 (1862). (8) Zaharia, *Cent.* **1896**, I 100

—— DI-(TRICHLOROMETHYL) CARBONATE  $C_3O_3Cl_6$ Beil. III - 17 III_1-(8) III_2-(16)

B.P. 203° at 760 mm. M.P. 78–79°

See 3:1915. *Division A: Solids.*

3:6315 *n*-BUTYL TRICHLOROACETATE $C_6H_9O_2Cl_3$ Beil. S.N. 160

n-$C_4H_9O.CO.CCl_3$

B.P.				
203–205°	(1)	D_4^{25} = 1.266 (3)	n_D^{25} = 1.4495 (3)
111°	at 40 mm. (2)		
100–101°	at 24 mm. (3)	D_4^{20} = 1.2778 (4)	n_D^{20} = 1.4525 (4)

[For prepn. (82–89% yield (3), 98% yield (2)) from n-butyl alc. (1:6180) + trichloroacetic ac. (3:1150) see (2) (3).]

3:6315 (1) Cheng, *Z. physik. Chem.* **B-24**, 308 (1934). (2) Liston, Dehn, *J. Am. Chem. Soc.* **60**, 1264–1265 (1938). (3) Waddle, Adkins, *J. Am. Chem. Soc.* **61**, 3361–3364 (1939). (4) Schjanberg, *Z. physik. Chem* **A-172**, 229 (1935).

3:6317 TRICHLOROACETALDEHYDE DIETHYLACETAL $C_6H_{11}O_2Cl_3$ Beil. I - 621
(β,β,β-Trichloroacetal) $Cl_3C—CH(OC_2H_5)_2$ I_1—
(Chloral diethylacetal) I_2—

B.P. 204.8° at 758.7 mm. (1) $D_{-}^{15.2} = 1.2655$ (1)
197° (2)
84–85° at 10 mm. (3)

Colorless oil, spar. sol. aq. (abt. 5 g. C̄ per liter aq. (2)), but misc. with alc., ether, or glycerol.

[For prepn. of C̄ from ethyl α,β,β,β-tetrachloroethyl ether [Beil. I-623, I_2-(681)] (itself prepd. (25–33% yield (3)) cf. (7) from chloral ethylalcoholate (3:0860) with PCl_5) by protracted boilg. (4) (5) (1) with abs. alc. (70% yield (3)) see indic. refs.; for formn. of C̄ from chloral ethylalcoholate (3:0860) with Cl_2 at 80° (2), or from 75% ethyl alc. with Cl_2 (2), see indic. refs.]

C̄ above 200° or on distn. with conc. H_2SO_4 yields (2) anhydrous chloral (3:5210).

C̄ is stable toward alkalies (2) and is unattacked by HCl gas even at 150° (6).

[C̄ with K *ter*-butylate in *ter*-butyl alc. splits out HCl giving (76% yield (3)) dichloroketene diethylacetal, b.p. 177° at 732–740 mm., $D_{25}^{25} = 1.1672$, $n_D^{25} = 1.4350$ (3).]

3:6317 (1) Paterno, Pisati, *Gazz. chim. ital.* **2**, 333–338 (1872). (2) Byasson, *Compt. rend.* **87**, 26 (1878); *Bull. soc. chim.* (2) **32**, 304–305 (1879). (3) Magnani, McElvain, *J. Am. Chem. Soc.* **60**, 2211–2212 (1938). (4) Wurtz, Frapolli, *Jahresber.* **1872**, 438. (5) Wurtz, Vogt, *Zeit für Chemie*, **1871**, 680. (6) Jacobsen, Neumeister, *Ber.* **15**, 602 (1882). (7) Post, *J. Org. Chem.* **6**, 833 (1941).

3:6318 β,β'-DICHLORO-ISOPROPYL ACETATE $C_5H_8O_2Cl_2$ Beil. II - 130
(Glycerol α,α'-dichlorohydrin β-acetate, β-aceto-α,γ-dichlorohydrin) II_1-(59) II_2-(140)

$CH_2Cl—CH(O.CO.CH_3)—CH_2Cl$

B.P. 205° (1) at 760 mm.	(2)	$D_4^{25} = 1.267$ (6)	$n_D^{25} = 1.4513$ (6)
202–208°	(3)		
204°	(13)	$D_{20}^{20} = 1.281$ (9)	$n_D^{20} = 1.4555$ (7)
202–203° at 740 mm.	(4)		1.4542 (9)
194–195° u.c.	(11)		
193–195°	(9)		
115–120° at 40 mm.	(5)		
108–110° at 40 mm.	(6)		
87–89° at 12 mm.	(7)		
86° at 12 mm.	(8)		
84.5° at 8 mm.	(10)		

[*See also β,γ-dichloro-n-propyl acetate* (3:6220).]

[For prepn. of C̄ from 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985) with AcCl (3:7065) under reflux (11) (9) (15) (3) or with Ac_2O (1:1015) (12) (13) in pres. of a trace of H_2SO_4 (8) see indic. refs.]

[For prepn. of C̄ from 3-chloro-1,2-epoxypropane (epichlorohydrin) (3:5358) with AcCl (3:7065) (73% yield (7)) in s.t. at 100° for 2 hrs. (10) or 30 hrs. (4) or with Ac_2O (1:1015) in s.t. at 180° for 4 hrs. (4) or in pres. of anhydrous $FeCl_3$ at ord. temp. for 24 hrs. (90% yield (14)) see indic. refs.]

{For formn. of C̄ from glycerol (1:6540) with AcCl (3:7065) (1) or with AcOH (1:1010) + HCl gas at 100° (1) or from glyceryl triacetate (triacetin) with HCl gas (5) see indic. refs.}

{C̄ with MeOH contg. 1% HCl at 60° for 6 hrs. gives (85% yield (7)) 1,3-dichloropropanol-2 ("α-dichlorohydrin") (3:5985); for study of rate of hydrolysis of C̄ with N/10 HCl see (15).}

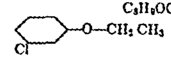
C̄ with K phthalimide at 150–170° for ½ hr., then extracted with AcOH, gives (3) β,β′-*bis*-(phthalimido)isopropyl acetate, m.p. 194° (3).

3:6318 (1) Berthelot, de Luca, *Ann. chim.* (3) **52**, 459–460 (1858). (2) Gibson, *J. Soc. Chem. Ind.* **50**, 950 (1931). (3) Fairbourne, Cowdrey, *J. Chem. Soc.* **1929**, 133–134. (4) Truchot, *Compt. rend.* **61**, 1171 (1865), *Ann.* **138**, 297–299 (1866); **140**, 244–246 (1866). (5) De La Acena, *Compt. rend.* **139**, 868 (1904). (6) Gibson, *J. Soc. Chem. Ind.* **50**, 973 (1931). (7) Sjöberg, *Svensk Kem. Tid.* **53**, 454–457 (1941); *Cent.* **1942**, II 25, *C.A.* **37**, 4363 (1943). (8) Wegscheider, Zmerslikar, *Monatsh.* **34**, 1075 (1913). (9) Humnicki, *Bull. soc. chim.* (4) **45**, 280 (1929). (10) Abderhalden, Weil, *Fermentforschung* **4**, 84 (1920), *Cent.* **1920**, III 643.

(11) Henry, *Ber.* **4**, 704 (1871). (12) Seelig, *Ber.* **24**, 3470 (1891). (13) Bigot, *Ann. chim.* (6) **22**, 492–493 (1891). (14) Knoevenagel, *Ann.* **402**, 134–138 (1914). (15) Bancroft, *J. Am. Chem. Soc.* **41**, 425, 429 (1919).

3:6323 *m*-CHLOROPHENETOLE C_8H_9OCl Beil. VI - 185

(*m*-Chlorophenyl ethyl ether) VI₁— VI₂—



B.P.

201–205° cor. at 717 mm. (1) $D_4^{20} = 1.1712$ (1)

201–205° (2)

Colorless oil with agreeable odor. — Eas. sol. alc., ether, AcOH, C_6H_6.

{For prepn. of C̄ from *m*-chlorophenol (3:0255) with EtI + KOH on alc. in s.t. at 100° for 3 hrs. see (1).}

{C̄ with HCN + C_6H_6 + $AlCl_3$ at room temp. for 2 hrs. followed by hydrolysis gives (80% yield (2)) 2-chloro-4-ethoxybenzaldehyde [Beil. VIII-81], m.p. 66.5° (2).}

The direct nitration of C̄ has not been reported. {Note, however, that all 4 possible mononitration products are known: viz., 3-chloro-2-nitrophenetole, m.p. 52° (3); 3-chloro-4-nitrophenetole, m.p. 39–40° (3); 3-chloro-5-nitrophenetole, m.p. 47° (4); and 3-chloro-6-nitrophenetole, m.p. 63° (3) (5), 62–63° (6). — The only known dinitro-derivative of C̄ is 3-chloro-4,6-dinitrophenetole [Beil. VI-259], m.p. 112° (7) (8). — The only known trinitro-derivative of C̄ is 3-chloro-2,4,6-trinitrophenetole [Beil. VI-292], m.p. 61° (5). — All 6 of these nitro products were obtained indirectly.}

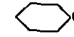
3:6323 (1) Wohlleben, *Ber.* **42**, 4372 (1909). (2) Gattermann, *Ann.* **357**, 349–350 (1907). (3) Hodgson, Clay, *J. Chem. Soc.* **1930**, 966. (4) van Erp, *J. prakt. Chem.* (2) **129**, 335 (1931). (5) Blanksma, *Rec. trav. chim.* **21**, 322, 325 (1901). (6) Beilstein, Kurbatow, *Ann.* **182**, 110 (1876). (7) Robert, *Rec. trav. chim.* **56**, 939 (1937). (8) Blanksma, *Rec. trav. chim.* **23**, 123 (1904).

—— 2,3-DICHLOROPHENOL $C_6H_4OCl_2$ Beil. VI —

VI₁-(102) VI₂—

B.P. 206° M.P. 58°

See 3:1175 Division A: Solids.

3:6327 BENZAL (DI)CHLORIDE  $CHCl_2$ $C_7H_6Cl_2$ Beil. V - 297
(Benzylidene (di)chloride, V_1-(152)
α,α-dichlorotoluene; V_2-(232)
ω,ω-dichlorotoluene)

B.P.	F.P.	
[207° cor. (1)]	−16.0° to −16.2° cor. (9)	D_4^{14} = 1.2557 (1)
	−16.1° cor. (10)	n_D^{20} = 1.5503 (8)
205.2° at 760 mm. (2)	−16.4° (11)	1.5502 (13)
205.15° at 760 mm. (3)	−17.0° (12)	
205° (37)	−17.4° (2)	D_4^0 = 1.2699 (4)
203.5° at 756.2 mm. (4)		$n_D^{19.4}$ = 1.5515 (14)
203.5° (5)		See Note 2. See Note 3.
201° (6)		
118° at 60 mm. (7)		
104–105° at 30 mm. (8)		
See Note 1.		

Note 1. The b.p. of 214° given by (15) appears without justification.

Note 2. $D_4^{56.8}$ = 1.2122 (4); $D_4^{79.2}$ = 1.1877 (4); $D_4^{135.5}$ = 1.1257 (4).

Note 3. The value of n_D^{20} for mixtures of C̄ with benzyl chloride (3:8535) (n_D^{20} = 1.5391 (13)) is a linear function of their composition (13).

[*See also benzyl chloride* (3:8535) *and benzotrichloride* (3:6540).]

Ordinary comml. C̄, usually obtd. by chlorination of toluene, frequently conts. benzyl chloride (3:8535) and benzotrichloride (3:6540), which are difficult (if not impossible) to remove by distillation methods. For purification of C̄ by repeated fractional freezing see (5); for patent on purification of C̄ from inorganic contaminants see (16). The best approach to pure C̄ is from benzaldehyde by action of PCl_5 (see below).

C̄ is insol. aq.; sol. alc., ether, or below −20° in equal vol. of pet. ether (17).

[For a method for quant. detn. of C̄ in mixtures with benzyl chloride (3:8535) and benzotrichloride (3:6540) see (18); for a rapid combustion method for detn. of chlorine in C̄ see (19).]

PREPARATION OF C̄

From benzaldehyde. [For prepn. of C̄ from benzaldehyde (1:0195) with PCl_5 (yield: 80–85% (20)) (21) in $CHCl_3$ (9), with $POCl_3$ in C_6H_6 (22), with $SOCl_2$ (23) (24), with $COCl_2$ (3:5000) in s.t. at 120–130° (25), with oxalyl (di)chloride (3:5060) in s.t. at 130–140° for 2 hrs. (26), or with succinyl (di)chloride (3:6200) in s.t. at 100° (27) see indic. refs.]

From toluene. [For prepn. of C̄ from toluene (1:7405) with SO_2Cl_2 (2 moles) in presence of a trace of dibenzoyl peroxide refluxed for 6 hours (90% yield (8)), with $SOCl_2$ in s.t. at 230–250° (28), with PCl_5 in s.t. at 190–195° for 2 hours (29), or with NOCl at 350° (30) see indic. refs.]

[For studies of formn. of C̄ from toluene (1:7405) with Cl_2, especially in light, see the scientific papers (13) (31) (32) (33) and patents (34) (35) (36).]

From other sources. [For formn. of C̄ from benzyl chloride (3:8535) with Cl_2 (37) (38), with NOCl at 150° (39), or with $PbCl_4.2NH_4Cl$ (40) see indic. refs.; from various benzyl ethers by cleavage with PCl_5 see (41); from α-chlorobenzyl chloroformate [Beil. VII-211] by loss of CO_2 on distn. see (42); or from benzaldazine with NOCl see (43).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Pyrolysis. [$\bar{C}$ passed over red-hot Pt wire gives (44) HCl and both *cis* (3:1380) and *trans* (3:4210) tolane dichlorides (*α,α′-dichloro-α,α′-diphenylethylenes*).]

Reduction. [$\bar{C}$ with H_2 in pres. of Pd/$CaCO_3$ (45) or Ni (46) in alc KOH loses all its halogen as HCl (use in quant. detn.) but the corresp. org. reduction prod. has not been characterized. — $\bar{C}$ with H_2 in pres. of colloidal Pd in dil alc. gives (47) toluene (1:7405), benzyl chloride (3:8535), and *α-stilbene dichloride* (3.4854). — $\bar{C}$ *in MeOH/KOH* with hydrazine hydrate in pres. of Pd gives (19% yield (48)) α-stilbene dichloride (3.4854).]

Hydrolysis. $\bar{C}$ upon hydrolysis yields benzaldehyde (1 0195) and HCl; frequently the reaction is so executed that the benzaldehyde reacts further according to the nature of the environment; examples of both types of reaction are cited below.

[$\bar{C}$ with aq. in s.t. at 140–160° (1), with aq in pres. of ferric salts (49) or metallic Fe (50) below 100°, with 50% aq. acetone at 72° (59), with conc. H_2SO_4 (2 moles) at 50° subsequently poured into aq. (51), with H_3BO_3 (1 mole) at 130–160° (52) (note that benzyl chloride (3:8535) is unaffected while benzotrichloride (3.6540) gives benzoic acid (1:0715)), with boilg. aq. K_2CO_3 (53), *with moist* $NiCO_3$ *at 120° or moist* $CoCO_3$ at 60° for 3 hrs. (60), with aq. Na_2SO_3 at 110° (54), with ZnO in C_6H_6 followed by aq. (55), with anhydrous formic acid (56) (57), or with anhydrous oxalic acid at 130° (58) gives (yields: 85% (52), 82% (58), 79% (51), 76% (60), 75% (59), 70% (54), 30% (55)) benzaldehyde (1:0195).]

[For study of kinetics of *hydrolysis of* $\bar{C}$ *at* 30° and 60° *in aq.* acetone either directly or in pres. of H_2SO_4 or KOH see (61), with aq. or KOH in 95% alc. see (62): for study of influence of substituents on hydrolysis of $\bar{C}$ see (61) (63) (64)]

[$\bar{C}$ with AcOH + $ZnCl_2$ gives (65) benzaldehyde (1·0195) + acetyl chloride (3:7065) + HCl. — $\bar{C}$ with anhydrous alkali acetate at 180–200° for 10–20 hrs. gives (66) cinnamic acid (1:0735) — $\bar{C}$ with AgOAc (32) (1) (67) or with PbO in AcOH (68) gives benzal diacetate [Beil VII-210, VII_1-(119)], m.p. 45–46°.]

Alcoholysis. [$\bar{C}$ with EtOH + $ZnCl_2$ gives (65) benzaldehyde (1:0195) + ethyl chloride (3:7015) + HCl; an analogous reaction occurs with $\bar{C}$ + $ZnCl_2$ + aromatic alcohols (69). — $\bar{C}$ with sodium alcoholates under ord. press. gives the corresp. benzaldehyde acetals: e g., $\bar{C}$ with MeOH/NaOMe at 100° for 15 hrs. gives (15% yield (70)) (67) benzaldehyde dimethylacetal [Beil. VII-209], b.p. 194–196°; $\bar{C}$ with EtOH/NaOEt at 100° for 24 hrs. gives (33% *yield* (70)) (67) benzaldehyde *diethylacetal* [Beil. VII-209, VII_1-(119)], b.p. 222°. — However, $\bar{C}$ with sodium alcoholates under press. in s.t. gives (70) benzaldehyde (1:0195) together with the corresp. alkyl chlorides.]

Substitution. *Chlorination* [$\bar{C}$ with Cl_2 in pres. of I_2 gives (32) *p*-chlorobenzal (di)-chloride (3:6700) — *Note, however, that* $\bar{C}$ with excess liquid Cl_2 in s.t. in sunlight gives (71) an addn. prod., viz., benzal (di)chloride hexachloride, m.p. 153° (71); *also that* $\bar{C}$ with NOCl at 150° substitutes in the side chain giving (39) benzotrichloride (3:6540). — Note further that $\bar{C}$ with SO_2Cl_2 + dibenzoyl peroxide does *not* react even when refluxed for 20 hrs. (8); cf. prepn. of $\bar{C}$ from toluene by this method (above).]

Bromination. [$\bar{C}$ with Br_2 in pres. of metallic beryllium gives (72) *p-bromobenzal (di)-bromide*, b p. 170–171° at 10 mm. (72). — $\bar{C}$ with Br_2 at 120–140° gives (57) benzodichloride bromide, $C_6H_4CCl_2Br$, b p. 88–94° at 1 mm., and benzochloride dibromide, $C_6H_5OClBr_2$, b p. 98–103° at 1 mm.]

Sulfonation. [$\bar{C}$ with SO_3 does *not* sulfonate but instead undergoes hydrolysis: e.g., $\bar{C}$ with sulfuric acid monohydrate at 35° gives (73) a mixt. of benzaldehyde-sulfonic *acids in* the ratio 10% *o-* + 30% *m-* + 60% *p-*, although these products cannot be isolated as such.]

Nitration. [All three isomeric mononitro derivatives *of* $\bar{C}$ are known, viz , *o*-nitrobenzal (di)chloride [Beil. V-332, V_1-(163)], m.p. 27.5° (63), 26–26.5° (61), 25 7° (11); *m*-nitrobenzal (di)chloride [Beil. V-332, V_1-(163), V_2-(254)], m.p. 64.5–65° (61), 64.5° (11); *p-nitrobenzal*

(di)chloride [Beil. V-332, V_1-(163), V_2-(255)], m.p. 43.0–43.5° (61), 43° (63), 42.8° (11); however, they are best prepared by reaction of the corresp. nitrobenzaldehydes with PCl_5 (74) (75). — For thermal anal. of mixtures of the three nitrobenzal (di)chlorides see (11). — For study of the mononitration of C̄ with anhydrous HNO_3 in Ac_2O at 20° giving about 23% *o*- + 34% *m*- + 43% *p*- see (11) cf. (76). — Note that neither dinitro nor trinitro derivatives of C̄ have been reported]

Behavior with other inorganic reactants. *C̄ with metals.* [C̄ with Na on htg gives (1) stilbene (1:7250). For behavior of C̄ with Na in liq. NH_3 giving dibenzyl, benzylamine, and other products see (80). — C̄ with equal wt. of Cu powder at 100° for 12 hrs. couples with loss of 2 Cl giving (77) α-stilbene dichloride (3:4854). — C̄ on boiling with Cu in aq Na_2CO_3 for 24 hrs. gives (78) benzaldehyde-copper, $2C_6H_5.CHO.Cu$, green cryst., decg. about 220° without melting. — C̄ with Cu in pyridine reacts vigorously (79), but the products have not been characterized.]

C̄ with inorganic salts. [C̄ with $AlCl_3$ in pet. eth. or CS_2 evolves HCl and resinifies (37); C̄ with very small amt. $AlCl_3$ at −15° gives (small yield (81)) phenyl-*m*-dichloromethylphenylchloromethane, b.p. 285° at 750 mm.]

[C̄ with SbF_3 on htg gives (82) (83) benzal (di)fluoride [Beil. V-290, V_1-(149), V_2-(224)], b.p. 139.95° (83), $D^{20}_{-} = 1.13572$ (84), $n^{20}_{D} = 1.45775$ (84).]

[C̄ with alc. Na_2S under N_2 gives (85) cf. (86) monomeric thiobenzaldehyde, but this cannot be isolated since it immediately undergoes polymerization to β-trithiobenzaldehyde and/or other reactions. — C̄ with alc. NaSH refluxed 3–4 hrs. gives (86) dibenzyl disulfide [Beil. VI-465, VI_1-(229), VI_2-(437)], m.p. 69–70° (86).]

[C̄ with conc. aq. NH_4OH on stdg. 4 months at ord. temp. (87), or C̄ with alc. NH_4OH in s t. at 100° (88), or C̄ with alc. NH_4OH + trace of Zn dust at room temp. (88), gives hydrobenzamide [Beil. *VII-215, VII_1-(120)*], m.p. *110°, doubtless through intermediate* hydrolysis to benzaldehyde since this can sometimes (88) be isolated.]

Behavior with organic reactants. *C̄ with hydrocarbons.* [C̄ with C_6H_6 in pres of $AlCl_3$ (37) (89), Cr (90), $BeCl_2$ at 130–140° for 20 hrs. (91), or Zn dust (92) undergoes Friedel-Crafts reaction giving (yields: 28.7% (91), 19.5% (90), 13.4% (37)) triphenylmethane (1:7220) frequently accompanied (37) (89) by other products such as diphenylmethane (1:7120) and triphenylchloromethane (3:3410). — C̄ with C_6H_6 + Al + $HgCl_2$ at 50–55° gives (93) cf. (89) 9, 10-diphenyl-9, 10-dihydroanthracene [Beil. V-745, V_2-(681)], m.p 164° *(89), 159° (93).]*

[C̄ with toluene in pres. of $BeCl_2$ refluxed 3 hrs. gives (73% yield (91)) phenyl-di-*p*-tolylmethane (4,4′-dimethyl-triphenylmethane) [Beil. V-712, V_1-(352), V_2-(623)], accompanied by other products. — C̄ with toluene + Al + $HgCl_2$ at 60–70° for 2 hrs. gives (93) a hydrocarbon $C_{28}H_{24}$, m.p. 185°, possibly having the structure 9,10-di-*p*-tolyl-9,10-dihydroanthracene.]

[C̄ with *o*-xylene (1:7430) + $AlCl_3$ in acetylene tetrachloride (3:5750) as solvent gives *(very small yield (94)) 2,3,6,7-tetramethyl-9,10-diphenylanthracene, m.p. 312°; note that* this product has composition $C_{30}H_{26}$ and is *not* a dihydroanthracene deriv.]

[For use of C̄ + conc. H_2SO_4 as a color test for various aromatic hydrocarbons see (95) (96).]

C̄ with phenols. [C̄ with phenol at 120° for 10 hrs. condenses with loss of HCl giving (87% yield (70)) 4,4′-dihydroxy-triphenylmethane (leucobenzaurin) [Beil. VI-1042, VI_1-(1010)], ndls. from aq alc. or from $CHCl_3$, m.p. 160–161° (corresp. diacetate, m p. 115° (97)): this prod. is also obtd. from benzaldehyde (1:0195) by condensation with phenol (1:1420) in pres. of H_2SO_4 (yields: 25% (98), 22% (99)) or H_3PO_4 (100): note that the isomeric benzaldehyde diphenylacetal is unreported. For formn. of resin from C̄ with phenol see (101).]

[$\bar{C}$ with 2 moles β-naphthol (*1:1540*) on htg. condenses with loss of $HCl + H_2O$ giving (97% yield (102)) (103) 9-phenyl-1,2,7,8-dibenzoxanthene [Beil. XVII-98], pr. or tbls. from AcOH, m.p. 190–191° (103), 190° (102); this prod is also obtd from benzaldehyde (1:0195) by condensation with β-naphthol in AcOH in s t. at 200° for 2 days (104) or in pres. of H_2SO_4 (104) at 100°; see also under benzaldehyde (1:0195) for use as test for latter.]

$\bar{C}$ with amines [$\bar{C}$ with aniline (2 moles) in pres. of Zn dust (92) or $BeCl_2$ at 120–125° for 2 hrs. (91) condenses giving (54% yield (91)) 4,4′-diamino-triphenylmethane [Beil XIII-274, $XIII_1$-(89)], cryst. from C_6H_6 with 1 mole solvent, m p. 106° (106), 104–105° (92), cryst. from dry ether without solvent, m p. 139–140° (106), 139° (107) (corresp. diacetyl deriv., m.p 233–234° (108) (109)); this compound is also obtd. from benzaldehyde (*1:0195*) *by condensation with 2 moles aniline in various ways, e g., see* (108) (106) (107).]

[$\bar{C}$ with *N,N*-dimethylaniline (2 moles) in pres of $ZnCl_2$ at 100° (110) condenses giving 4,4′-*bis*-(dimethylamino)-triphenylmethane (*leuco*-Malachite Green) [Beil. XIII-275, $XIII_1$-(89)], cryst. from C_6H_6 or alc in 3 forms, m p 102° (111) (112), m p. 93–94° (111), 92–93° (112), and 77° (112) cf (111); this prod is also obtd. from benzaldehyde (1:0195) *by condensation with 2 moles N,N-dimethylaniline in various ways, e.g., with $ZnCl_2$ at 100°* (113) (112), or with $POCl_3$ (alm. 100% yield (114))]

[For study of reactivity of $\bar{C}$ toward pyridine or piperidine see (115).]

$\bar{C}$ with other nitrogenous reactants [$\bar{C}$ (excess) with thiourea at not above 150° gives (116) (117) a salt, $C_9H_9N_3S_2$ HCl, m p. 236° (117), regarded as 4,6-di-imino-2-phenyl-*1,3,5-dithiazane (117). — For analogous behavior of $\bar{C}$ with N-phenylthiourea and with* *N*-(*p*-tolyl)-thiourea see (117)]

[$\bar{C}$ with Zn salt of *o*-aminophenyl mercaptan in AcOH/NaOAc refluxed 30 min. in current of H_2S gives (low yield (118)) 2-phenylbenzothiazole, m.p. 114° cor.]

$\bar{C}$ with organometallic reactants [$\bar{C}$ with MeMgI gives (22% yield (119)) α-stilbene *dichloride* (3:4854) + ethane but no isopropylbenzene (cumene) or *sym.*-dimethyldiphenylethane; however, $\bar{C}$ with MeMgCl gives (120) no α-stilbene dichloride but instead a mixture of four other compds., viz, isopropylbenzene (cumene) (1:7440), 1-chloro-1,2-diphenylpropane, and two forms of 2,4-diphenylbutane.]

[$\bar{C}$ with C_6H_5MgBr gives (119) cf. (121) triphenylmethane (1:7220) + α-stilbene dichloride (3:4854) + biphenyl (1:7175)]

[$\bar{C}$ with Me_2Zn gives (122) isopropylbenzene (cumene) (1:7440).]

[$\bar{C}$ does not react with Hg di-*p*-tolyl even on refluxing in toluene for 300 hrs (123).]

Ⓟ **Hydrolysis to benzaldehyde:** $\bar{C}$ on boilg. with 10% K_2CO_3 soln. gives benzaldehyde *(1:0195); after acidification with HCl the benzaldehyde may be detected with fuchsin* aldehyde reagent. (Dif. from *pure* benzyl chloride (*3:8535*) or *pure* benzotrichloride (3.6540).)

Ⓓ **Benzaldehyde phenylhydrazone:** m.p. 156° u.c. [From $\bar{C}$ with 3 moles phenylhydrazine refluxed in alc for 2 hrs. (55% yield (124)); note that from the mother liquor small amounts of an isomeric (γ) benzaldehyde phenylhydrazone, m.p. 154–155°, are obtd. (124).]

Ⓓ **Benzaldehyde semicarbazone:** m p. 219–220° u.c. (124). [From $\bar{C}$ (3.2 g.) with semicarbazide hydrochloride (4.4 g) + Na_2CO_3 (2.1 g.) refluxed a few hrs. in alc. and the ppt. recrystd. from hot aq. (124); note that the m.p. of this prod. varies somewhat with rate of htg. cf. (1:0195).]

3:6327 (1) Limpricht, *Ann.* **139**, 317–321 (1866). (2) Timmermans, *Bull. soc. chim. Belg.* **25**, 334–343 (1913); *Cent* **1914**, I 618. (3) Lecat, *Ann soc. sci Bruxelles* **B-47**, 68 (1927); *Cent.* **1927**, II 905, *C.A.* **22**, 4296 (1928). (4) Schiff, *Ber.* **18**, 503 (1886). (5) Olivier, Weber, *Rec. trav. chim.* **53**, 880 (1934). (6) Lock, Asinger, *Monatsh.* **59**, 157 (1932). (7) Lauer, *J. prakt. Chem.* (2) **142**, 257 (1935). (8) Kharasch, Brown, *J. Am. Chem. Soc.* **61**, 2146 (1939). (9) Sutton,

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42, 3976 (1909). (27) Rembold,
5). (29) Colson, Gautier, *Ann.*
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31, 3150–3157. (32) Beilstein, Kuhlberg, Neuhof, *Ann.* **146**, 322–323, 327 (1868). (33) Beilstein, *Ann.* **116**, 336–341 (1860).
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–312 (1903).
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(1907). (44) Löb, *Ber.* **36**,
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143 (1899). (50) Schultze,

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18,232, Feb. 16, 1881,
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1913, 1074–1093
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(88) Böttinger,
Chakrabarty, D
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(91) Brederock, Lehmann, Schönfeld, Fritzsche, *Ber.* **72**, 1415–1419, 1423 (1939). (92) Böttinger, *Ber.* **12**, 976 (1879). (93) Ray, *J. Chem. Soc.* **117**, 1336, 1338 (1920). (94) Barnett,

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(111) E. Fischer, O. Fischer, O. Lehmann, *Ber.* **12**, 798 (1879). (112) Heertjes, Bakker, van Kerkhof, *Rec. trav. chim.* **62**, 738–739 (1942). (113) Fischer, *Ann.* **206**, 122–129 (1880). (114) Nencki, *Monatsh.* **9**, 1148–1149 (1888). (115) Tronov, *J. Russ. Phys.-Chem. Soc.* **58**, 1278–1301 (1926); *Cent.* **1927**, II 1145–1146, *C.A.* **22**, 2737 (1928). (116) Abel, *Am. Chem. J.* **13**, 118–119 (1891). (117) Underwood, Dains, *J. Am. Chem. Soc.* **57**, 1769–1770 (1935). (118) Bogert, Stull, *J. Am. Chem. Soc.* **47**, 3081 (1925). (119) Fuson, Ross, *J. Am. Chem. Soc.* **55**, 720–722 (1933). (120) Ellingboe, Fuson, *J. Am. Chem. Soc.* **55**, 2960–2964 (1933).

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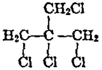
3:6335 1,2,3-TRICHLORO-2(CHLOROMETHYL) PROPANE

$C_4H_6Cl_4$ Beil. I —
I_1—
I_2-(89)



B.P. **206–210°** cor. (1)
87° at 9 mm. (2)

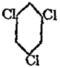
D_4^{25} = **1.481** (1) n_D^{20} = **1.508** (1)

Colorless odorless oil (2).

[For formn. of $\bar{C}$ (together with other products) from *ter*-butyl chloride (3:7045) + Cl_2 see (1); from 3-chloro-2-(chloromethyl)propene-1 (3:5633) in $CHCl_3$ by shaking with Cl_2/aq. see (2).]

3:6335 (1) Rogers, Nelson, *J. Am. Chem. Soc.* **58**, 1028 (1936). (2) Kleinfeller, *Ber.* **62**, 1595 (1929).

—— 1,3,5-TRICHLOROBENZENE



$C_6H_3Cl_3$ Beil. V - **204**
V_1-(**113**)
V_2-(**156**)

B.P. **208°** M.P. **63°**

See 3:1400. *Division A: Solids.*

3:6345 2,3-DICHLOROTOLUENE

$C_7H_6Cl_2$ Beil. V - **295**
V_1—
V_2—

B.P. **207–208°** at 760 mm. (1)
204–206° at 755 mm. (2)
61–62° at 3 mm. (8)

n_D^{20} = **1.5511** (8)

[For prepn. of $\bar{C}$ from 2-chloro-3-aminotoluene [Beil. XII-870, XII_1-(404)] via diazotization and use of Cu_2Cl_2 reaction (alm. quant. yield (2), 64% (8)) see indic. refs.; for formn. of $\bar{C}$ (together with other dichlorotoluenes) from toluene or *o*-chlorotoluene (3:8245) with Cl_2 in pres. of $FeCl_3$ or $MoCl_5$ see (3) (4), from *o*-chlorotoluene + Cl_2 + Al/Hg see (4).]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg gives (70% yield (5)) 2,3,4-trichlorotoluene (3:0425), m.p. 41°.] [$\bar{C}$ with Br_2 at 180–200° gives (8) 2,3-dichlorobenzal (di)bromide (not isolated) which on hydrolysis with conc. H_2SO_4 gives (71% yield (8)) 2,3-dichlorobenzaldehyde (3:1480).]

$\bar{C}$ on mononitration with conc. HNO_3 (6) or cold mixt. of 2 pts. conc. HNO_3 + 3 pts. conc. H_2SO_4 (2) yields 2,3-dichloro-4-nitrotoluene [Beil. V-332], ndls. from alc. + AcOH, m.p. 50.5–51.5° (2), 51° (6); $\bar{C}$ on dinitration with mixt. of 7 pts. fumg. HNO_3 + 3.5 pts. conc. H_2SO_4 yields (2) 2,3-dichloro-4,6-dinitrotoluene [Beil. V-345], cryst. from AcOH or alc., m.p. 71–72° (2).

$\bar{C}$ on oxidn. with alk. $KMnO_4$ (6) or with dil. HNO_3 for some hrs. in s.t. at 140° (2) (6) yields 2,3-dichlorobenzoic acid (3:4650), m.p. 166° (6), 163° (2).

$\bar{C}$ on sulfonation with 2 pts. 10% oleum at 50° gives (7) mixt. of 89% 2,3-dichlorotoluenesulfonic acid-6 (corresp. sulfonyl chloride, m.p. 51–52° (7), corresp. sulfonamide, m.p. 228° (7)) and 11% 2,3-dichlorotoluenesulfonic acid-5 (corresp. sulfonyl chloride, m.p. 87° (7), corresp. sulfonamide, m.p. 185° (7)).

3:6345 (1) Wynne, Greeves, *Proc. Chem. Soc.* **11**, 151 (1895). (2) Cohen, Dakin, *J. Chem. Soc.* **79**, 1128–1129 (1901). (3) Seelig, *Ann.* **237**, 157, 166 (1887). (4) Ref. 2, pp. 1114–1117. (5) Cohen, Dakin, *J. Chem. Soc.* **81**, 1339–1340 (1902). (6) Ref. 3, pp. 162–163 (7) Silvester, Wynne, *J. Chem. Soc.* **1936**, 692–694. (8) Marvel, Overberger, Allen, Johnston, Saunders, Young, *J. Am. Chem. Soc.* **68**, 861–862 (1946).

3:6355 3,4-DICHLOROTOLUENE

$C_7H_6Cl_2$

Beil. V - 296
V_1-(152)
V_2—

B.P.			F.P.	
207–208.1° cor. at	**770 mm.**	**(1)**	**−16.0° (1)**	D^{20}_{20} = **1.2541 (1)**
208.3–208.8°	**at 745.5 mm.**	**(2)**		**1.2512 (4)**
205.5–206.5°		**(3)**		n^{22}_D = **1.5490** (1)
200.5°	**u.c. at 741 mm.**	**(4)**		

For f.p./compn. diagram of system: $\bar{C}$ + 2,4-dichlorotoluene (3:6290) see (1); the eutectic conts 52% $\bar{C}$ and freezes about −38° (1).

[For prepn. of $\bar{C}$ from 4-chloro-3-aminotoluene [Beil. XII-871, XII_1-(404)] by diazotization and Cu_2Cl_2 reactn. (77% yield (5)) see (5) (6); similarly from 3-chloro-4-aminotoluene [Beil. XII-989, XII_1-(436)] see (4) (3) (1); from 2-chloro-4-methylphenol (3:6215) with PCl_5 see (7); from salts of 3,4-dichlorotoluenesulfonic acid-2 or 3,4-dichlorosulfonic acid-5 by hydrolysis see (8).]

[For formn. of $\bar{C}$ (42% together with 58% 2,4-dichlorotoluene (3:6290)) from *p*-chlorotoluene (3:8287) with Cl_2 in pres. of Fe see (1); for formn. of $\bar{C}$ (together with other isomers) from toluene with Cl_2 in pres. of I_2 (9) (10) or of $MoCl_5$ (11) (12) or with SO_2Cl_2 at 160° (13) see indic. refs.; for formn. of $\bar{C}$ (together with other isomers) from *m*-chlorotoluene (3:8275) or *p*-chlorotoluene (3:8287) with Cl_2 in pres. of Al/Hg see (14).]

[$\bar{C}$ with Cl_2 in pres. of Al/Hg yields exclusively (15) 2,4,5-trichlorotoluene (3:2100), m.p. 81–82° (15); $\bar{C}$ at its b.p. treated with Cl_2 yields (16) (5) (17) 3,4-dichlorobenzal dichloride (3:6876), b.p. 257°.

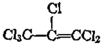
$\bar{C}$ on mononitration with mixt. of 2 pts. conc. HNO_3 + 4 pts. conc. H_2SO_4 yields (6) (18) 3,4-dichloro-6-nitrotoluene [Beil. V-331], ndls. from alc. + AcOH, m.p. 63–64° (6) (19), 63° (20); $\bar{C}$ on dinitration yields (6) 3,4-dichloro-2,6-dinitrotoluene [Beil. V-345], ndls. from AcOH, m.p. 91.5–92.5° (6) (19).

$\bar{C}$ on oxidn. (2) with CrO_3 (9) (10), with $KMnO_4$ (21), or with dil. HNO_3 in s.t. at 130–150° (4) (6) (8) yields 3,4-dichlorobenzoic acid (3:4925), m.p. 206°.

[$\bar{C}$ on sulfonation with fumg. H_2SO_4 yields (6) 3,4-dichlorotoluenesulfonic acid-6 (corresp. sulfonyl chloride, m.p. 81° (6), 82° (22), corresp. sulfonamide, m.p. 190–191° (6), 189° (22)); note, however, that the isomeric derivs., viz., 3,4-dichlorotoluenesulfonyl chloride-2, m.p. 49° (8), and 3,4-dichlorotoluenesulfonamide, m.p. 186° (8), have been independently prepd.]

3:6355 (1) Wahl, *Compt. rend* **202**, 2161–2163 (1936); *Bull. soc. chim.* (5) **4**, 344–349 (1937). (2) Kraay, *Rec. trav. chim.* **49**, 1085, 1090 (1930). (3) Wynne, *J. Chem. Soc.* **61**, 1059–1060 (1892). (4) Lellmann, Klotz, *Ann.* **231**, 312–314 (1885). (5) Ruggli, Zaeslin, Lang, *Helv. Chim. Acta* **21**, 1248 (1938). (6) Cohen, Dakin, *J. Chem. Soc.* **79**, 1133 (1901). (7) Schall, Dralle. *Ber.* **17**, 2535 (1884). (8) Wynne, *J. Chem. Soc.* **1936**, 702, 705. (9) Beilstein, Kuhl- [illegible] (1875). [illegible] 263 (1877). (13) [illegible] Cohen, Dakin, *J.* [illegible] (17) Booth, Elsey, [illegible] *Chim. Acta* **19**, 437 [illegible], Tod, Witham, *J. Chem. Soc.* **127**, 2348 (1925).
(21) Bornwater, Holleman, *Rec. trav. chim.* **31**, 228–229 (1912). (22) Silvester, Wynne, *J. Chem Soc.* **1936**, 692.

3:6370 HEXACHLOROPROPENE



C_3Cl_6 Beil. I - 200
I_1-(83)
I_2—

B.P.
209–210° at 760 mm. (1) (2)
122–123° at 50 mm. (1)
99° at 15 mm. (2)

D_4^{20} = **1.7652** (1) n_D^{20} = **1.5091** (1)

Oil with fragrant odor. — Insoluble aq.

[For prepn. of $\bar{C}$ from *sym.*-heptachloropropane (3:6860) by loss of HCl in presence of $AlCl_3$ in CCl_4 at 60–70° (83% yield) see (3); from *asym*-heptachloropropane (3:0200) by htg. at 250–420°, especially in presence of $ZnCl_2$ or CuCl (4) (with latter tetrachloroethylene (3:5460), is also formed (4) (5)), or by htg with alc. KOH at 50–60° (90% yield (6)) (1); from heptachloro-*n*-butyraldehyde [Beil. I_1-(346)] by actn. of 2 moles NaOEt see (7).]

$\bar{C}$ with $AlCl_3$ + 1 mole trichloroethylene (3.5170) in CH_2Cl_2 (3:5020) or $CHCl_3$ (3:5050) at 30–37° gives (82% yield (6)) 1,1,2,3,3,4,5,5,5-nonachloropentene-1, colorless liq. with cedar-like odor, b.p. 128° at 2–3 mm., 86° at 0.2 mm., D_{20}^{20} = 1.812, n_D^{20} = 1.5703 (6): with excess trichloroethylene (3:5170) prod. is mixt. consisting exclusively of two dodecachloroheptenes, $C_7H_2Cl_{12}$, one m p. 94–96°, the other, m.p. 58–62° (6).

$\bar{C}$ with $AlCl_3$ + 1,2-dichloroethylene (3:5030) in CH_2Cl_2 soln. yields (8) a single 1,1,2,3,- [illegible] 13–113.5° at 2 mm., D_{21}^{21} = 1.749, [illegible] (80% yield (8)) a mixt. of penta- [illegible]

$\bar{C}$ forms with $AlCl_3$ at 80° a yel. cryst. addn.-prod. sparingly sol. in CCl_4 but regenerating $\bar{C}$ upon treatment with aq. (8).

$\bar{C}$ on cautious warming with conc. H_2SO_4 (9) (10) (2) (11) or on boilg. with an aqueous suspension of $BaCO_3$ (2) yields α,β,β-trichloroacrylic acid (3:1840) spar. sol. cold aq., eas. sol. hot aq., pr. from CS_2, m.p. 76° (2).

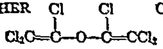
$\bar{C}$ does not add Br_2 (10), but $\bar{C}$ in sunlight adds Cl_2 yielding (10) octachloropropane (3:4450) q.v.

$\bar{C}$ with alc. NaOEt yields (1) triethyl *ortho*-α,β,β-trichloroacrylate, b.p. 236–237°, D_4^{20} = 1.2183, n_D^{20} = 1.4649 (1). [This *ortho* ester on htg. with 2 vols. conc. HCl yields (1) ethyl α,β,β-trichloroacrylate, b.p. 192–194°, D_4^{20} = 1.3740, n_D^{20} = 1.4889 (1), which can be hydrolyzed by conventional methods to α,β,β-trichloroacrylic acid (see above).]

3:6370 (1) Fritsch, *Ann.* **297**, 314–316 (1897). (2) Böeseken, Dujardin, *Rec. trav. chim.* **32**, 98–100 (1913). (3) Prins, *Rec. trav. chim.* **54**, 251–252 (1935). (4) Böeseken, van der Scheer, de Voogt, *Rec. trav. chim.* **34**, 78–95 (1915). (5) Böeseken, *Rec. trav. chim.* **45**, 467–468 (1915). [illegible] Schimmel, *Rec. trav. chim.* **32**, 122 Prins, *Ger.* 261,689, July 2, 1913; 6 (1914).

3:6373 DI(TRICHLOROVINYL) ETHER

C_4OCl_6 Beil. I - 725, I_1—, I_2—



B.P. 210° (1) D_-^{21} = **1.654 (1)**

[For prepn. of $\bar{C}$ from decachlorodiethyl ether (3:1676) by treatment with alc. K_2S see (1).]

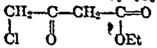
$\bar{C}$ with Cl_2 in sunlight adds 2 moles halogen yielding (1) decachlorodiethyl ether (3:1676), m.p. 69°.

$\bar{C}$ with Br_2 in sunlight adds 2 moles halogen yielding (1) *bis*-(α,β-dibromo-α,β,β-trichloroethyl) ether, m.p. 96° (1).

3:6373 (1) Malaguti, *Ann. chim.* (3) **16**, 19–28 (1846).

3:6375 ETHYL γ-CHLOROACETOACETATE
(Ethyl γ-chloro-β-keto-*n*-butyrate)

$C_6H_9O_3Cl$ Beil. III - 663, III_1-(233), III_2-(426)



B.P.			F.P.		
210° dec.		(1)	**−5°** (2) (9)	D_4^{20} = **1.2157** (4)	
205° dec.		(2) (9)	**−8°** (1)		
117–119°	**at 17 mm.**	(3)		D_4^{17} = **1.2176** (4)	n_D^{17} = **1.4540** (4)
107°	**at 14 mm.**	(4)			**1.45452** (1)
105°	**at 11 mm.**	(2) (9)			
102°	**at 12 mm.**	(1)		D_4^{16} = **1.2182** (4)	
103°	**at 12 mm.**	(19)			
92–93°	**at 6 mm.**	(19)			
80°	**at 3 mm.**	(19)			

[*See also ethyl α-chloroacetoacetate* (3:6207).]

Colorless limpid liq. which soon turns yellow (4). — Almost insol. aq. but miscible with most org. solvents. — [Note that purity of material of earlier workers (5) has been seriously questioned (2).]

[For prepn. of $\bar{C}$ from acetylketene (ketene dimer (6) (7)) by conversion with Cl_2 to γ-chloroacetoacetyl chloride (3:9088) and reactn. of the latter with excess abs. EtOH at 0° see (3); from ethyl chloroacetate (3:5700) (2 moles) with Mg (1 mole) in dry ether contg. $HgCl_2$ (56% yield (1)) cf. (19) or with Mg in dry ether contg. I_2 (35% yield (4)) or with

Al/Hg in pres. of a trace of EtOH (8) see indic. refs.; from chloroacetaldehyde (3:7212) with ethyl diazoacetate see (5); from ethyl γ-chloro-β-hydroxy-n-butyrate [Beil. III-310, III_1-(116)] by careful oxidn. with $K_2Cr_2O_7 + H_2SO_4$ (poor yield) see (9).]

$\bar{C}$ on hydrolysis with aq. HCl for 3 hrs undergoes ketonic splitting yielding (1) chloroacetone (3:5425) + CO_2 + EtOH (note that this does not distinguish $\bar{C}$ from *ethyl α-chloroacetoacetate which yields same products*).

[$\bar{C}$ with alc. NaOEt at 100° undergoes bimolecular condensation with loss of 2 HCl yielding (10) diethyl succinylosuccinate [Beil. X-894, X_1-(434)], m.p. 125–126° (10); this same condensation is also effected by other alkaline agents, e.g., sodium phenolate, dil. aq. NaOH, NH_4OH, NH_3 in ether, KOAc alone or in pres. of alc. or C_6H_6, diethyl sodiomalonate or Me_2NH in C_6H_6, or K phthalimide (10).]

[$\bar{C}$ with ethyl orthoformate (1:3241) in Ac_2O refluxed for ½ hr. ppts. on cooling (45% yield (11)) ethyl γ-chloro-α-ethoxymethylene-acetoacetate, colorless ndls. from alc. or C_6H_6, m.p 98° (11).]

Note that $\bar{C}$ is capable of displaying keto-enol tautomerism as is shown by the following reactions:

$\bar{C}$ with $FeCl_3$ soln. gives red coloration (1) (4) (9) (19); $\bar{C}$ conts. 10.9% enol, but 4% soln. of $\bar{C}$ in ether conts. 53% enol. (19).

$\bar{C}$ forms a series of metallic salts of the enolic form; these are in general insol. in aq. but soluble in org solvents: e.g., $Cu(C_6H_8O_3Cl)_2$ (from $\bar{C}$ on shaking with aq. $Cu(OAc)_2$), green ndls. from C_6H_6, m.p. 168–169° dec. (9) (4) cf. (19), 167.5° dec. (1), 163° (8); $Mg(C_6H_8O_3Cl)_2$ (from $\bar{C}$ shaken with aq. $MgSO_4 + NH_4Cl$), m.p. 170° (1); $Zn(C_6H_8O_3Cl)_2$ (from $\bar{C}$ on shaking with $NH_4OH/ZnSO_4$), m.p. 121° (1); $Ni(C_6H_8O_3Cl)_2$ (from $\bar{C}$ on shaking with $Ni(OAc)_2 + NH_4OH$), m.p. 131–132° (1); other metals behave similarly (1).

$\bar{C}$ couples with *diazonium salt solns. in pres. of NaOAc yielding the corresp. α-(arylhydrazones)* of ethyl γ-chloro-α,β-diketo-n-butyrate (ethyl γ-chloro-α-(arylazo)acetoacetates (cf. dif. behavior of isomeric ethyl α-chloroacetoacetate (3:6207)): e.g., $\bar{C}$ with benzenediazonium chloride soln. in pres. of NaOAc at 0° gives (12) (13) ethyl γ-chloro-β-keto-α-phenylhydrazono-n-butyrate, sparing sol. yel. ndls. from alc., m.p. 92–93° (12) (13), 92° (14) (note that this prod. on htg. with alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-phenylpyrazole, colorless pr. from alc., m.p. 85° (14) (15)); similarly $\bar{C}$ with p-nitrobenzenediazonium chloride soln. in pres. of NaOAc at 0° gives (16) ethyl γ-chloro-α-(p-nitrobenzeneazo)acetoacetate, yel. ndls. from alc., m.p. 135° (16) (note that this prod. with hot alc. KOAc loses HCl and ring-closes to 3-carbethoxy-4-hydroxy-1-(p-nitro)phenylpyrazole, colorless ndls. from AcOH, m.p. 220° (16). — [For analogous reactions of $\bar{C}$ with numerous other diazonium salts see the papers represented by (16) (14) (17).]

$\bar{C}$ with thiourea on warming in alc. for 4 hrs. loses HCl and ring-closes yielding (9) ethyl (2-aminothiazolyl-4)acetate, colorless cryst. from C_6H_6, m.p. 94° (18), 74° (9) (one of these is probably a misprint for the other).

3:6375 (1) Hamel, *Bull. soc. chim.* (4) **29**, 390–402 (1921). (2) Lespieau, *Bull. soc. chim.* (4) **9**, 31–33 (1911). (3) Hurd, Abernathy, *J. Am. Chem. Soc.* **62**, 1147–1148 (1940). (4) Alexandrow, *Ber.* **46**, 1021–1024 (1913). (5) Schlotterbeck, *Ber.* **42**, 2570–2571 (1909). (6) Boese, *Ind. Eng. Chem.* **32**, 16–22 (1940). (7) Hurd, Williams, *J. Am. Chem. Soc.* **58**, 962–968 (1936). (8) Picha, Doht, Weisl, *Monatsh.* **27**, 1245–1249 (1906). (9) Lespieau, *Bull. soc. chim.* (3) **33**, 463–464 (1905); *Compt. rend.* **138**, 422 (1904). (10) Sommelet, Couroux, *Bull. soc. chim.* (4) **29**, 402–406 (1921).

(11) Benary, Ebert, *Ber.* **56**, 1897–1898 (1923). (12) Favrel, *Compt. rend.* **145**, 196 (1907). (13) Favrel, Prevost, *Bull. soc. chim.* (4) **49**, 245–246 (1931). (14) Chattaway, Lye, *Proc. Roy. Soc. London* **A-137**, 492, 497, 501 (1932). (15) Wolff, *Ann.* **313**, 15 (1900). (16) Chattaway, Ashworth, *J. Chem. Soc.* **1933**, 1146. (17) Chattaway, Lye, *Proc. Roy. Soc. London* **A-135**,

294-295 (1932). (18) Steude, *Ann.* **261**, 30-31 (1891). (19) Arndt, Loewe, Capuano, *Rev. faculté sci. univ. Istanbul* **8-A**, 122-152 (1943); *C.A.* **39**, 1626 (1945).

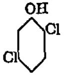
—— *d,l-α,β*-DICHLOROPROPIONIC ACID $C_3H_4O_2Cl_2$ **Beil. II - 252, II₁-(111), II₂—**

$$CH_2—CH—COOH$$
Cl Cl

B.P.	M.P.
210° sl. dec. at 762 mm.	49-50°

See 3:0855. *Division A: Solids.*

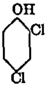
—— 2,5-DICHLOROPHENOL $C_6H_4OCl_2$ **Beil. VI - 189, VI₁-(103), VI₂-(178)**



B.P. 211° at 744 mm. **M.P. 58°**

See 3:1190. *Division A: Solids.*

—— 2,4-DICHLOROPHENOL $C_6H_4OCl_2$ **Beil. VI - 189, VI₁-(103), VI₂-(178)**



B.P. 211° **M.P. 45°** $D_{-}^{25} = 1.4723$ $n_D^{25} = 1.1729$

See 3:0560. *Division A: Solids.*

3:6380 ETHYL *α,α,β*-TRICHLORO-*n*-BUTYRATE $C_6H_9O_2Cl_3$ **Beil. II - 281, II₁—, II₂—**

$$CH_3.CH—C(Cl)—COOC_2H_5$$
Cl Cl

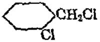
B.P. 212°		(1)	$D_{25}^{25} = 1.3094$ (2)
174.2° cor.	at 250 mm.	(2)	$D_{20}^{20} = 1.3138$ (2)
101.5°	at 17 mm.	(3)	$D_{15}^{15} = 1.3183$ (2)

[For prepn. of Č from α,α,β-trichloro-*n*-butyric acid (3:1280) in EtOH with 10% conc. H_2SO_4 in s.t. at 100° for 3 days see (2); note that the acid esterifies with difficulty and attempts to use the dry HCl method give only very poor yields (2).]

Č with Zn dust in moist ether loses HCl giving (almost 100% yield (3)) ethyl α-chlorocrotonate (3:8523).

3:6380 (1) Judson, *Ber.* **3**, 787 (1870). (2) Perkin, *J. Chem. Soc.* **65**, 424 (1894). (3) Michael, Schulthess, *J. prakt. Chem.* (2) **43**, 594-596 (1891).

3:6400 o-CHLOROBENZYL CHLORIDE $C_7H_6Cl_2$ Beil. V - 297 V_1-(152) V_2-(231)



B.P. 213–214°		(1)
105–107°	at 28 mm.	(2)
109.0–109.2°	at 25.6 mm.	(3)
110°	at 24 mm.	(4)
94°	at 15 mm.	(5)
96–98°	at 14 mm.	(4)
94–95°	at 10 mm.	(6)
84–85°	at 3 mm.	(4)

[For prepn. of C̄ from o-chlorobenzyl alcohol [Beil. VI-444, VI_1-(222)] with PCl_5 (7) or with $SOCl_2$ + pyridine (5) see indic. refs.; from o-chlorotoluene (3:8245) with $PbCl_4$.-$2NH_4Cl$ (1) or with Cl_2 (8) (9) in ultra-violet light (4) see indic. refs.; from benzyl chloride (3:8535) with Cl_2 see (10).]

[For condens. of C̄ with p-chlorophenol and use of prod as anti-moth prepn. see (11); for use in prepn. of condensation prod. with sulfonated phenol see (12).]

[C̄ with phenol in toluene yields (13) 2-(o-chlorobenzyl)phenol, b.p. 146–151° at 3 mm. (benzoate, b.p. 173–176° at 2.5 mm.), and o-chlorobenzyl phenyl ether, b.p. 140–145° at 2.5 mm., C̄ with 2,4-dichlorophenol (3:0560) in toluene yields 2-(o-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.5–60.5° (benzoate, m.p. 81–82°), and o-chlorobenzyl 2,4-dichlorophenyl ether, m.p. 61–62°.]

[C̄ with phenol + $AlCl_3$ yields (13) 4-(o-chlorobenzyl)phenol, m.p. 68–69° (benzoate, m.p. 64.5–65.5°), and 2-(o-chlorobenzyl)phenol (see above); C̄ with 2,6-dichlorophenol (3:1595) + $AlCl_3$ yields (13) 4-(o-chlorobenzyl)-2,6-dichlorophenol, m.p. 86.5–87.5° (benzoate, m.p. 86–87°).]

[C̄ with Mg in 10 moles dry ether gives (60–75% yield (4)) cf. (25) $o\text{-}Cl.C_6H_4.CH_2MgCl$ (particularly sensitive to air oxidn.); this with CO_2 followed by acidification or with methyl chloroformate (3:5075) followed by hydrolysis yields (4) o-chlorophenylacetic acid, m.p. 94–95° (3:2640); the R.MgCl cpd. with phenyl isocyanate as directed (22) for p-isomer should yield o-chlorophenylacetanilide [Beil. XII-275], m.p. 140° cor. (23), 138.5° (24), although this method has not been specifically reported for C̄; the RMgCl cpd. with $HgCl_2$ gives (25) o-chlorobenzyl HgCl, m.p. 111°, or with $HgBr_2$ gives (25) o-chlorobenzyl HgBr, m.p. 128°.]

[For study of behavior of C̄ with NaOEt see (14) (7); for study of rate of reaction of C̄ with LiI, NaI, or KI (6) (5) or with Na_2SO_3 (2) see indic. refs., for study of acid hydrolysis of C̄ in various solvents see (5); for reaction of C̄ with KCN yielding o-chlorobenzyl cyanide (which on hydrolysis gives o-chlorophenylacetic acid (3:2640)) see (15) (16); for behavior of C̄ with cellulose (17) or sodium cellulose (18) see indic. refs.]

C̄ refluxed 4 hrs. with hexamethylenetetramine (1 mole) in 60% alc. soln. yields (19) o-chlorobenzaldehyde (3:6410) q.v.; C̄ htd. in xylene with p-nitrophenylhydrazine yields (20) o-chlorobenzal-p-nitrophenylhydrazone, m.p. 241° (20).

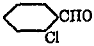
C̄ on mononitration with 1.2 pts. fumg. HNO_3 at 30–40° gives (35% yield (21)) 2-chloro-5-nitrobenzyl chloride, pr. from alc., m.p. 66° (21).

3:6400 (1) Seyewetz, Trawitz, *Compt. rend.* **136**, 241 (1903). (2) Sprung, *J. Am. Chem. Soc.* **52**, 1640–1649 (1930). (3) de Bruyne, Davis, Gross, *J. Am. Chem. Soc.* **55**, 3938 (1933). (4) Austin, Johnson, *J. Am. Chem. Soc.* **54**, 657 (1932). (5) Bennett, Jones, *J. Chem. Soc.* **1935**, 1818. (6) Conant, Hussey, *J. Am. Chem. Soc.* **47**, 486 (1925). (7) Olivier, *Rec. trav. chim.* **41**, 308–309 (1921). (8) Jones, *J. Chem. Soc.* **1935**, 1839. (9) Zelinsky & Schering-Kahlbaum, Ger. 478,084, June 20, 1929; *Cent.* **1929**, II 1216. (10) Olivier, *Rec. trav. chim.* **41**, 419–421 (1921).

(11) [illegible]
320,056
Huston
(14) Fr
J. Biol. Chem. 58, 220 (1923). (16) Mehner, *J. prakt. Chem.* (2) 62, 554-555 (1900). (17) Niethammer, König, *Cellulosechem.* 10, 201-205 (1929). (18) Ball, Hibbert, *Can. J. Research* 7, 481-498 (1932). (19) Mayer, English, *Ann.* 417, 78 (1918). (20) Busch, Lang, *J. prakt. Chem.* (2) 144, 312 (1936).

(21) Meisenheimer, Zimmermann, von Kummer, *Ann.* 446, 225-226 (1926). (22) Underwood, Gale, *J. Am. Chem. Soc.* 56, 2117-2119 (1934). (23) Jenkins, Richardson, *J. Am. Chem. Soc.* 55, 1619 (1933). (24) Mehner, *J. prakt. Chem.* (2) 62, 558 (1900). (25) Ware, Hixon, *J. Am. Chem. Soc.* 60, 1262-1263 (1938).

3:6410 *o*-CHLOROBENZALDEHYDE C_7H_5OCl Beil. VII - 233 VII₁-(132)



B.P.		M.P.		
213-214°	(1) (2) (14)	11° (4)	$D_4^{20} = 1.2512$ (6)	$n_D^{20} = 1.56708$ (6)
209.7-211.7° at 760 mm.	(3)			
208° at 748 mm.	(4)			
205-206° cor. at 740 mm.	(5)			
96.0-96.6° at 16 mm.	(3)			

Oil, volatile with steam. — C̄ often contains *o*-[illegible]benzyl chloride (3:6400) as impurity (7). — C̄ very easily oxidized in air (probabl[illegible]use of variant constants). — C̄ yields $NaHSO_3$ cpd. (15) (21).

[For prepn. of C̄ from *o*-chlorotoluene (3:8245) with $MnO_2 + H_2SO_4$ (8), or PbO_2 (24% yield (21)), or CrO_2Cl_2 in CCl_4 (9) or CS_2 (10), or via halogenation to *o*-chlorobenzal (di)chloride (3:6625) (5) (12) or *o*-chlorobenzal (di)bromide (11) and subsequent hydrolysis with fumg. H_2SO_4 (11) (12) (1) or anhydrous oxalic ac. (14) see indicated refs.; for prepn. from *o*-nitrobenzaldehyde via *o*-aminobenzaldehyde see (12); from *o*-chlorobenzyl alc. by dehydrogenation with CuO + dinitrobenzene in quinoline (86% yield) see (13); from *o*-chlorobenzyl chloride (3:6400) [illegible] chloride (3:6640) by cat. reduc[illegible] formalin + hexamethylenetetramine see (1); for other misc. methods see [illegible]

C̄ with CrO_3 (16) or $KMnO_4$ (2) oxidizes to *o*-chlorobenzoic acid (3:4150), m.p. 141°. [For study of auto-oxidn. see (17).] — C̄ on cat. hydrogenation gives (yield: 90% (18); 50% (19)) *o*-chlorobenzyl alc., m.p. 69° (19), 64-65° (18). — C̄ with conc. alk. undergoes Cannizzaro reactn. (for study on dioxane soln. see (20)) although presumable products, *o*-chlorobenzyl alc. and *o*-chlorobenzoic acid, have not (by this reactn.) actually been isolated.

C̄ with dil. alc. KCN for 4 hrs. at 60° gives (21% yield (22)) 2,2′-dichlorobenzoin, m.p. 63-64° (22). — C̄ with KCN + HCl yields *o*-chloromandelonitrile which on hydrolysis with HCl gives *o*-chloromandelic acid, m.p. 84-85° (23).

C̄ on htg. with NaOAc + Ac_2O for 8 hrs. at 180-200° undergoes Perkin reactn. giving (71% yield (12)) *o*-chlorocinnamic acid, m.p. 211° (12). [This with Br_2 in $CHCl_3$ gives (24) *o*-chlorocinnamic acid dibromide, m.p. 183° (24).] — C̄ + malonic acid + pyridine gives (38) alm. quant. yield of *o*-chlorocinnamic ac., m.p. 211-212° (31). [In absence of pyridine reactn. gives 93% yield *o*-chlorobenzalmalonic acid, m.p. 102° (37).]

C̄ on mononitration as specified (25) gives 2-chloro-5-nitrobenzaldehyde, cryst. from

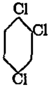
dil. AcOH, m.p. 78–79° (25), 80° (26). [Oxime, m.p. 147–148° (26); *corresp.* acid, 2-chloro-5-nitrobenzoic acid, m.p. 165° (25).]

C̄ in alc. warmed at 58–60° for 2 hrs. with $(NH_4)_2CO_3$ + KCN as directed (37) gives 5-(*o*-chlorophenyl)hydantoin, m.p. 175.7–176.1° cor. (37).

[C̄ with hydrazine sulfate gives (91–95% yield (40)) *o*-chlorobenzaldazine, m.p. 143.5° cor., but C̄ with hydrazine hydrate gives (84% yield (40)) *o*-chlorobenzaldehyde hydrazone m.p. 33–34°, b.p. 165–170° at 14 mm.; note that latter on Wolff-Kishner reduction gives (35–82% yield (40)) *o*-chlorotoluene (3:8245).]

- Ⓓ *o*-Chlorobenzaldoxime (*anti* form): pr. from alc., m.p. 75–76° (1) (27). [From C̄ + $NH_2OH.HCl$ + Na_2CO_3 (1); the *sym.* isomer has m.p. 98–102° (28), 101–103° (7).]
- Ⓓ **o-Chlorobenzaldehyde phenylhydrazone**: m.p. 86° (29), 84° (39).
- Ⓓ **o-Chlorobenzaldehyde p-nitrophenylhydrazone**: or. pl., m.p. 249° (30) (31); br.-red. ndls., 241° (32); red ndls. from alc., 237–238° (13).
- Ⓓ **o-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone**: or.-red. ndls. from xylene, m.p. 209° (33), 213.6° (34) 207° (41). [Use in detn. of C̄ (11).]
- Ⓓ **o-Chlorobenzaldehyde dimethone**: ndls. from alc., m.p. 199° u.c., 205° cor. (35). [Corresp. anhydride, cryst. from alc., m.p. 224–226° cor. (35).]
- Ⓓ **o-Chlorobenzaldehyde semicarbazone**: lfts. from MeOH, m.p. 229–230° (36), tbls. from pyridine, m.p. 225–226° (9), 226° (42).

3:6410 (1) Erdmann, Schwechten, *Ann.* **260**, 55–58 (1890). (2) Mayer, English, *Ann.* **417**, 78 (1918) (3) Kahovec, Kohlrau[illegible]
werke, Ger. 207,157; *Cent.* **1909**, I
von Auwers, *Ann* **422**, 166 (1921
(1925) (8) Gilliard, Monet, Car
Chem Soc **93**, 1636 (1908). (10)
(11) Eitel, Lock, *Monatsh.* **72**, 3[illegible] (12) Bock, Lock, Schmidt, *Monatsh.* **64**, 406 (1934). (13) Zetsche, Zala, *Helv. Chim. Acta* **9**, 288–290 (1926). (14) Erdmann, Kirchhoff, *Ann* **247**, 368 (1888). (15) Rosenmund, Zetsche, *Ber.* **54**, 436–437 (1921). (16) Henry, *Ber.* **2**, 136 (1869). (17) van der Beek, *Rec. trav chim.* **51**, 411–413 (1932). (18) Carothers, Adams, [illegible]
(20) Eitel,
[illegible] nn. **478**, 128
(24) Will-
[illegible]) Erdmann,
[illegible] Chem. Soc. **125**, 551 (1924). (28) Behrend,
[illegible], Frohlich, *Cent.* **1903**, II 427. (30) Chattaway,
[illegible] Chem. Ind. **45**, T 91–93 (1926). (32) Busch, Lang, *J. prakt. Chem.* (2) **144**, 312 (1936). (33) Blanksma, Wacker, *Rec. trav. chim.* **55**, 658 (1936). (34) Ferrante, Bloom, *Am. J. Pharm.* **105**, 381–384 (1933). (35) Vorländer, *Z. anal. Chem.* [illegible] (1929) (36) Henderson, Heilbron, *J. Chem. Soc.* [illegible]
Chem Soc. **64**, 522–523 (1942). (38) K
14-A, 112–[illegible]
(40) Lock,
(41) Gra
5–11 (1943. [illegible] (42) Vogelsang, *Rec. trav. chim.* **62**,

3:6420 1,2,4-TRICHLOROBENZENE (*unsym.*-trichlorobenzene)  $C_6H_3Cl_3$ Beil. V - 204; V_1-(112); V_2-(156)

B.P.		M.P.		
213° cor.	(1) (17)	17–18°	(8)	D_{25}^{25} = 1.4634 (15)
212.9–213°	(2)	17°	(7) (9)	cf. (7)
212–213°	(3)	16–17°	(4)	n_D^{25} = 1.5524 (15)
211° cor. at 742 mm.	(4)	16.6°	(10)	
210°	(5) (6)	16.5°	(11) (12)	
206°	(7)	16°	(1) (3) (13)	
		14.5°	(14)	

For thermal anal. of mixts. of C̄ with 1,2,3-trichlorobenzene (3:0990) or with 1,3,5-trichlorobenzene (3:1400) see (10) (the eutectic of C̄ with the former conts. 71% C̄ and melts 2.7° (10)); for m.p./compn. data on ternary mixt. of C̄ with the other two isomers see (10).

[For use of C̄ in mfg. of elec. insulating material see (16).]

[For prepn. of C̄ from 2,4-dichloroaniline [Beil. XII-621; XII_1-(309)] (1) (11), from 2,5-dichloroaniline [Beil. XII-625, XII_1-(311)] (6), or 3,4-dichloroaniline [Beil. XII-626 XII_1-(311)] (1) via diazotization and use of Cu_2Cl_2 reaction see indic. refs.; from 4-chloro-1,3-diaminobenzene [Beil. XIII-53, $XIII_1$-(15)] via tetrazotization and use of Cu_2Cl_2 reaction (62% yield) see (17); from *p*-dichlorobenzene (3:0980) with S_2Cl_2 in SO_2Cl_2 + $AlCl_3$ (58% yield C̄) see (3) (18).]

[For formn. of C̄ from 2,3,6-trichlorobenzaldehyde (3:2287) by KOH fusion (88% yield (4)) or from 2,3,6-trichloroacetophenone by KOH fusion (82% yield (14)) see indic. refs.; from 2,4-dichlorophenol (3.0560) by htg. 7 hrs. with PCl_5 (25.5% yield) see (1); from 2-nitro-1,4-dichlorobenzene or from 4-chloro-3-nitrobenzenesulfonic acid by htg. with $SOCl_2$ in s.t. 10 hrs. at 160–180° see (19) (20); from 2-chlorobenzene-1,4-disulfonyl chloride with PCl_5 in s.t. 4 hrs. at 210° see (8); from 2,4-dichlorobenzenesulfonyl chloride by htg. with $SOCl_2$ in s.t. at 180° see (21).]

[For formn. of C̄ (together with other products) from C_6H_6 with Cl_2 in pres. of I_2 (7) or of Fe (22) see indic. refs.; from *o*-dichlorobenzene (3:6055) and/or *p*-dichlorobenzene (3:0980) with Cl_2 under various conditions see (22) (23) (24) (25) (9); from *m*-dichlorobenzene (3:5960) with Cl_2 under various conditions see (9) (13) (23); from chlorobenzene (3:7903) or *p*-dichlorobenzene (3:0980) by boilg. with $FeCl_3$ see (26); from α-benzenehexachloride (3:4410) on htg. above its m.p. (158°) (28) (21) or htd. with aq. in s.t. at 200° (27), or on boilg. with MeOH/KOH (10), EtOH/KOH (10) (28) (5) (22), alc. KCN (27), or pyridine (10), or on htg. with quinoline at 105–110° (10), see indic. refs.; from β-benzenehexachloride (3:4990) q.v. on boilg. with alc. KOH see (10).]

[C̄ with Cl_2 in pres. of Al/Hg yields exclusively (23) 1,2,4,5-tetrachlorobenzene (3:4115), m.p. 135–136° (23); C̄ with liq. Cl_2 in s.t. at room temp. for 10 days gives (29) (30) a mixt. of addn. products.]

[C̄ with NaOMe in MeOH under various conditions (31) (32) (33) (11) (34) yields 2,5-dichlorophenol (3:1190), m.p. 57°; for behavior with EtOH/KOH see (38).]

C̄ on mononitration, e.g., by soln. of C̄ (1 g.) in 5 ml. fumg. HNO_3 (D = 1.49) (35), then pouring onto ice (35), gives 100% yield (35) (1) (5) (15) (39) 1,2,4-trichloro-5-nitrobenzene [Beil. V-246], pr. from alc., m.p. 58° (1), 57° (7) (15), 56° (35); this prod. with piperidine as directed (36) yields 1,2-dichloro-4-piperidino-5-nitrobenzene, red pr. from alc., m.p. 64–65° (36).

$\bar{C}$ on dinitration, e.g., by soln. of $\bar{C}$ (1 g.) in 5 ml. fumg. HNO_3 ($D = 1.49$) + 5 ml. conc. H_2SO_4 and subsequent refluxing for 1 hr., then pouring into aq. (35), gives (100% yield (35)) (7) (37) 1,2,4-trichloro-3,5-dinitrobenzene [Beil. V-266], pr. from alc., m.p. 103.5° (7), 102.5–103.5° (35) (37); this prod. (1 g.) htd. 1 hr. at 100° with 5 g. aniline as directed (35) yields 1-chloro-2,4-dianilino-3,5-dinitrobenzene, m.p. 182° (35).

Note that the trinitration prod. to be expected from complete nitration of $\bar{C}$ has not been reported.

[$\bar{C}$ with chlorosulfonic acid as directed (35) yields 1,2,4-trichlorobenzenesulfonyl chloride, m.p. 31–34° (35) which with $(NH_4)_2CO_3$ yields 1,2,4-trichlorobenzenesulfonamide, m.p. above 200° (35).]

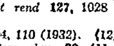
3:6420 (1) Beilstein, Kurbatow, *Ann.* **192**, 230–232 (1878). (2) Dadieu, Pongratz, Kohlrausch, *Monatsh* **61**, 433 (1932). (3) Silberrad, *J. Chem. Soc.* **121**, 1015–1020 (1922). (4) Lock, *Ber.* **66**, 1531 (1933). (5) Lesimple, *Ann.* **137**, 122–124 (1866). (6) Noelting, Kopp, *Ber.* **38**, 3509 (1905). (7) Jungfleisch, *Ann chim.* (4) **15**, 264–277 (1868). (8) Olivier, *Rec. trav. chim.* **39**, 502 (1920). (9) Mouneyrat, Pouret, *Compt rend* **127**, 1028 (1898). (10) van der Linden, *Ber.* **45**, 231–247 (1912)

(11) van der Lande, *Rec. trav. chim.* **51**, 104, 110 (1932). (12) Hassel, Naeshagen, *Z. physik. Chem.* **B-12**, 87 (1931). (13) Olivier, *Rec trav. chim.* **39**, 411–413 (1920). (14) Lock, Böck, *Ber.* **70**, 924 (1937). (15) T [illegible]
Cent. **1928**, I 2370, *C A* **22** [illegible]
U S. 2,139,945–2,139,948, I [illegible]
Cohn, Fischer, *Monatsh.* **21** [illegible]
1923; *Cent.* **1925**, I 904. ([illegible]
Ger. 280,739, *Cent.* **1915**, I 104.

(21) Quilico, *Gazz chim ital* **57**, [illegible]
Zil'berman, Slobodnik, *J. Applied* [illegible]
(1938); *C.A.* **32**, 1664 (1938) (23) [illegible]
Britton (to Dow Chem. Co), *U S.* [illegible]
(1933). (25) Slobodnik, Zil'berma [illegible]
Thomas, *Compt. rend.* **126**, 1212 (1898) (27) Meunier, *Ann. chim.* (6) **10**, 223–269 (1887). (28) Matthews, *J. Chem. Soc.* **59**, 165–172 (1891). (29) van der Linden, *Rec. trav. chim.* **55**, 315–324 (1936) (30) van der Linden, *Rec trav. chim.* **57**, 217–224 (1938).

(31) Holleman, *Rec. trav. chim.* **37**, 201 (1918) (32) Kraay, *Rec trav chim.* **49**, 1087 (1930). (33) de Crauw, *Rec. trav. chim* **50**, 787 (1931) (34) Aktien-Gesell, fur Anilin Fabrikation, Ger. 349,794, March 9, 1922, *Cent* **1922**, IV 45. (35) Huntress, Carten, *J. Am. Chem. Soc.* **62**, 512–514 (1940). (36) LeFevre, Turner, *J. Chem. Soc* **1927**, 1116–1117. (37) Hüffer, *Rec. trav. chim.* **40**, 452 (1920). (38) Clark, Crozier, *Trans. Roy. Soc Can.* (3) **19**, III 153–156 (1925). (39) Holleman, van Haeften, *Rec. trav chim.* **40**, 71 (1921).

—— *p*-CHLOROBENZYL CHLORIDE $C_7H_6Cl_2$ Beil. V - 297

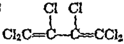


V_1-(152)
V_2-(231)

B.P. 214° **M.P. 29–30°**

See 3:0220. *Division A: Solids.*

3:6425 HEXACHLOROBUTADIENE-1,3 C_4Cl_6 **Beil. S.N. 12**



B.P.		M.P.		
215°	(1)	**−21°** (1) (2)	D_4^{20} = **1.6820** (1)	n_D^{20} = **1.5542** (1)
211° at 710 mm. (2)		**−19°** (5)		

[*See also octachlorocyclopentene* (3:0422).]

Colorless oily liq. with weak turpentine-like odor.

[For prepn. of C̄ from butadiene-1,3 (1) (3) or butane, butene, or their chloro substitution products (3) (4) with Cl_2; or from hexachlorobutene (itself obtd. from dimerization (5) (2) of trichloroethylene (3:5170)) by cat. addn. of Cl_2 followed by cat. removal of 2 HCl or vice versa (1) (2); or from acetylene with Cl_2 (6) (note that tetrachloroethylene (3:5460) is also formed).]

C̄ on reduction with Zn + alc. gives (1) butadiene-1,3 (corresp. tetrabromide, m.p. 117°).

C̄ behaves as if saturated: e.g., C̄ does *not* add Cl_2 (even in sunlight) (1); C̄ does *not* (1) react with maleic anhydride or benzoquinone-1,4; C̄ does *not* (1) polymerize (even at 100 atm.).

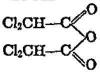
C̄ is stable toward acids and alkalies and (unlike some other highly chlorinated unsaturates) does *not* give a carboxylic acid on treatment with conc. H_2SO_4 (1).

Note that a product of m.p. 38° and b.p. 283° formerly regarded as C̄ is now thought to be octachlorocyclopentene (3:0390).

3:6425 (1) Fruhwirth, *Ber.* **74**, 1700–1701 (1941). (2) Consortium für Elektrochem. Ind., French 836,719, Jan. 25, 1939; *Cent.* **1939**, I 3256; [*C.A.* **33**, 5548 (1939)]: Ger. 723,981, July 2, 1942; [*C.A.* **37**, 5415 (1934)]. (3) Fruhwirth (to Donau-Chemie, A.G.), Ger. 736,884, May 20, 1943; *C.A.* **38**, 2974 (1944). (4) Wimmer, Mugdan (to Consortium für Elektrochem. Ind), Ger. 734,682, March 25, 1943; *C.A.* **38**, 1245 (1944). (5) Mugdan, Wimmer (to Consortium für Elektrochem. Ind.), Ger. 704,179, Feb. 20, 1941; *C.A.* **36**, 1116 (1942); U.S. 2,269,600, Jan. 13, 1942; *C.A.* **36**, 2870 (1942). (6) Fruhwirth (to Donau-Chemie, A.G.), Ger. 734,722, March 25, 1943; *C.A.* **38**, 1252 (1944).

3:6430 DICHLOROACETIC ACID ANHYDRIDE $C_4H_2O_3Cl_4$ Beil. II - 204

II_1—
II_2—



B.P.
214–216° dec. (1)
140° at 35 mm. (2)
100–102° at 16 mm. (3)

D^{24}_{-} = **1.574 (1)**

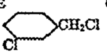
Note that the above name of C̄ is so rendered to emphasize that it is the anhydride of dichloroacetic acid (not a dichlorinated acetic anhydride).

[For prepn. of C̄ from dichloroacetyl chloride (3:5290) with NaĀ in $POCl_3$ in dry ether (1), or with NaĀ + $AlCl_3$ (4), or on boilg. with Na_2CO_3 (2) see indic. refs.; for formn. of C̄ as by-product during reactn. of sodium dichloroacetate with acetyl chloride (3:7065) in dry ether see (3) (the other prod. is the mixed anhydride, acetic-dichloroacetic anhydride [Beil. II-204], b.p. 79–80° at 16 mm., D^{20}_4 = 1.5170 (3).]

C̄ on hydrolysis with aq. yields dichloroactic acid (3:6208) q.v.; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see dichloroacetic acid (3:6208).

3:6430 (1) Anthoine, *Jahresber.* **1883**, 1032. (2) Patterson, *Ber.* **38**, 212–213 (1905). (3) Baroni, *Gazz. chim. ital.* **63**, 30 (1933); *Cent.* **1933**, I 3183; *C.A.* **27**, 3447 (1933). (4) Strosacker, Schwegler (to Dow Chem. Co.), U.S. 1,713,104, May 14, 1929; *Cent.* **1929**, II 1215; *C.A.* **23**, 3234 (1929).

3:6445 *m*-CHLOROBENZYL CHLORIDE $C_7H_6Cl_2$ Beil. V —
V₁—
V₂-(231)



B.P.

215–216°	at 753 mm.	(1)	$D_4^{15} = 1.2695$ (1)
213–214°	at 740 mm.	(2)	
111.0–111.2°	at 25.4 mm.	(3)	
111–113°	at 25 mm.	(4)	
110–111°	at 25 mm.	(5)	
104°	at 17 mm.	(6)	

[For prepn. from *m*-chlorobenzyl alc. [Beil. VI-444] with PCl_5 (1) or with $SOCl_2$ (yield: 87% (5), 78% (4)) see indic. refs.; from *m*-chlorotoluene (3:8275) with Cl_2 see (2) (3) (6) (7) (8) (9) see indic. refs.]

[C̄ with phenol in toluene yields (10) *o*-(*m*-chlorobenzyl)phenol, b.p. 192–194° at 14 mm. (benzoate, m.p. 67–67.4°), and *m*-chlorobenzyl phenyl ether, m.p 36.0–36.4°; C̄ with 2,-4-dichlorophenol (3:0560) in toluene yields (10) 2-(*m*-chlorobenzyl)-4,6-dichlorophenol, m.p. 59.4–60 0° (benzoate, m.p. 63 5–64.0°, benzenesulfonate, m.p. 114.5–115.0°, *p*-toluenesulfonate, m.p. 125.4–126.0°), and *m*-chlorobenzyl 2,4-dichlorophenyl ether, m p. 42–42.5°.]

[C̄ with phenol + $AlCl_3$ yields (10) *p*-(*m*-chlorobenzyl)phenol, b.p 145–148° at 3 mm. (benzoate, m.p. 57.5–58.0°); C̄ with 2,6-dichlorophenol (3:1595) yields (10) 4-(*m*-chlorobenzyl)-2,6-dichlorophenol, m.p. 79–80° (benzoate, m.p. 130–130.4°; *p*-toluenesulfonate, m.p. 104.5–105.0°).]

[C̄ with Mg in dry ether yields (8) *m*-$Cl.C_6H_4.CH_2Cl$; this on treatment with CO_2 yields *m*-$Cl.C_6H_4.CH_2.COOMgCl$ which on subsequent further treatment with various other RMgX cpds. undergoes abnormal reaction giving *m*-chlorophenylmalonic acid, m.p. 127–128° (8); the RMgCl cpd. with phenyl isocyanate as directed (13) for the *p*-isomer should yield *m*-chlorophenylacetanilide, m.p. 130° cor. (14), although this reaction has not been specifically reported for C̄.]

[For studies of rate of reaction of C̄ with NaOEt see (1) (11) (5); with Na_2SO_3 see (4); with $AlCl_3 + C_6H_6$ see (12); for acid hydrolysis in acetone see (6); with KI in various solv. see (6); for reactn. of C̄ with diethyl malonate see (2).]

3:6445 (1) Olivier, *Rec. trav. chim.* **41**, 309 (1921). (2) Kenner, Witham, *J. Chem. Soc.* **119**, 1460 (1921). (3) de Bruyne, Davis, Gross, *J. Am. Chem. Soc.* **55**, 3938 (1933). (4) Sprung, *J. Am. Chem. Soc.* **52**, 1643, 1649 (1930). (5) Franzen, Rosenberg, *J. prakt. Chem.* (2) **101**, 334 (1921). (6) Bennett, Jones, *J. Chem. Soc* **1935**, 1818. (7) Jones, *J Chem Soc.* **1935**, 1839. (8) Ivanov, Pchenitchny, *Bull. soc. chim.* (5) **1**, 231 (1934). (9) Zelinsky, Schering-Kahlbaum, Ger. 478,084, June 20, 1929; *Cent.* **1929**, II 1216. (10) Houston, Guile, Chen, Headley, Warren, Baur, Mate, *J. Am. Chem. Soc.* **55**, 4639–4643 (1933).

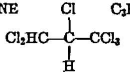
(11) Olivier, *Rec. trav. chim.* **41**, 650 (1921). (12) Olivier, Berger, *Rec. trav chim.* **45**, 717 (1926). (13) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117–2119 (1934). (14) Jenkins, *J. Am. Chem. Soc.* **55**, 2898 (1933).

— *m*-CHLOROPHENOL C_6H_5OCl Beil. VI - 185
VI₁-(99)
VI₂-(172)

B.P. 216° M.P. 32° $D^{50} = 1.237$ $n_D^{40} = 1.5565$

See 3:0255. *Division A: Solids.*

3:6460 1,1,1,2,3,3-HEXACHLOROPROPANE $C_3H_2Cl_6$ Beil. I —
(*unsym.*-Hexachloropropane) I_1-(35)
I_2—



B.P. 216° (1)		D_4^{24} = **1.6980** (1)	n_D^{17} = **1.5250** (1)
145° cor. at 90 mm. (1)			

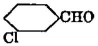
Colorless liq. [For use as solvent for cellulose esters see (3) (4).]

[For prepn. of C̄ from chloroform (3:5050) + trichloroethylene (3:5170) + $AlCl_3$ (1) (2) or from CCl_4 (3:5100) + 1,2-dichloroethylene (3:5030) + $AlCl_3$ see (1) (2).]

C̄ with 1 ml. alc. KOH loses HCl yielding (1) (2) 1,1,2,3,3-pentachloropropene-1 (3:6075), b.p. 183° (1).

3:6460 (1) Prins, *J. prakt. Chem.* (2) **89**, 417–419 (1914). (2) Prins, Ger. 261,689, March 2, 1912; *Cent.* **1913**, II 394; *C.A.* **7**, 3641 (1913). (3) Spicers, Ltd. & Hands, Brit. 279,139, April 21, 1926; *Cent.* **1928**, I 770; *C.A.* **22**, 2840 (1928). (4) Spicers, Ltd. & Hands, French 625,165, Aug. 4, 1927; *Cent.* **1928**, I 770.

3:6475 *m*-CHLOROBENZALDEHYDE C_7H_5OCl Beil. VII - 234
VII_1-(133)



B.P.		M.P.	
216.3–216.8° (1)		**17–18°** (2)	$D_4^{20.2}$ = **1.2410** (6)
213–214° (2)		**13°** (1) (2)	$n_D^{20.2}$ = **1.55908** (6)
210.5–211.5° at 740 mm. (3)			
107–109° at 26 mm. (4)			
98.6–100.2° at 16 mm. (5)			
84–86° at 8 mm. (4)			

Oil. — Volatile with steam. — C̄ yields $NaHSO_3$ cpd.

[For prepn. of C̄ from *m*-nitrobenzaldehyde via reductn. with $SnCl_2$ to *m*-aminobenzaldehyde followed by diazotization and reactn. with CuCl (yield: 75–79% (4), 70–80% (3), 58–65% (7) (24) see indic. refs.; from *m*-chlorotoluene (3:8275) with CrO_2Cl_2 (44.5% yield) see (8); from *m*-chlorobenzyl alc. by oxidn. with HNO_3/H_2SO_4 see (9); for formn. (together with other products) during chlorination of benzaldehyde see (10); from *m*-chlorobenzylamine with formalin + hexamethylenetetramine see (25).]

C̄ is readily oxidized even by air (4); C̄ with $KMnO_4$ yields *m*-chlorobenzoic acid (3:4392), m.p. 154°. [For study of auto-oxidn. see (11).] — C̄ with conc. NaOH undergoes Cannizzaro reactn. (for study in dioxane soln. see (23)) although the presumable products, *m*-chlorobenzyl alc., b.p. 234°, and *m*-chlorobenzoic acid, m.p. 154°, have not (by this reactn.) actually been isolated.

C̄ with dil. alc. KCN at 60° for 5 hrs. in absence of air gives 22% yield of 3,3′-dichlorobenzoin, cryst. from lgr., m.p. 75–76° (12).

C̄ on htg. with NaOAc + Ac_2O for 8 hrs. at 180–200° undergoes Perkin reactn. giving (61.5% yield (13)) *m*-chlorocinnamic acid, m.p. 165° (13) (14). [This with Br_2 in $CHCl_3$ gives dibromide, m.p. 183° (15).] — C̄ htd. with malonic acid + pyridine (24) gives alm. quant. yield (24) of *m*-chlorocinnamic acid, m.p. 163° (24). [In absence of pyridine reaction gives 100% yield *m*-chlorobenzalmalonic acid, m.p. 184–186° (24).]

C̄ on mononitration as specified (3) yields 3-chloro-6-nitrobenzaldehyde [Beil. VII-262], ndls. from dil. alc., m.p. 77.5° (3). [Oxime, tbls. from alc., m.p. 112° (3); phenylhydrazone, ndls. from alc., m.p. 180–181° (3).]

Ⓓ *m*-Chlorobenzaldoxime (*anti* form): pr. from alc., m.p. 70–71° (2), 70° (16) (17). [From C̄ + $NH_2OH.HCl$ + Na_2CO_3 (2); the *syn* isomer (from the *anti* via ethereal HCl, then Na_2CO_3) has m.p. 115–116° rap. htg. (2), 118° (17).].

Ⓓ *m*-Chlorobenzaldehyde phenylhydrazone: ndls. from abs. alc., m.p. 134–135° (3), 133–134° (18).

Ⓓ *m*-Chlorobenzaldehyde *p*-nitrophenylhydrazone: cryst. from dil. AcOH, m.p. 216° (19), 214° (16). [For m.p./compn. data on mixt. of this deriv. with benzaldehyde *p*-nitrophenylhydrazone, m.p. 190°, see (16).]

Ⓓ *m*-Chlorobenzaldehyde 2,4-dinitrophenylhydrazone: or.-yel. cryst., m.p. 256° (20), Bordeaux-red cryst. from xylene, m.p. 248° cor. (22), 245° (25). [Use in detn. of C̄ (22).]

Ⓓ *m*-Chlorobenzaldehyde semicarbazone: lfts. from MeOH (21) or pyridine (8), m.p. 230° (21), 228° (8). [This deriv. does not distinguish C̄ from *o*- (3:6410) or *p*- (3:0765) isomers.]

3:6475 (1) C
58–62 (1890)
Coll. Vol. 2
(1937). (6)
(8) Law, Perkin, *J. Chem. Soc* **93**, 1636–1637 (1908). (9) Mettler, *Ber.* **38**, 2812 (1905). (10) Gnehm, Bänziger, *Ann.* **296**, 65 (1897), *Ber.* **29**, 875 (1896).
(11) van der Beek, *Rec. trav chim* **51**, 412–413 (1932). (12) Weissberger, *J. Chem. Soc.* **1935**, 225. (13) Böck, Lock, Schmidt, *Monatsh.* **64**, 406 (1934). (14) Reich, Araus, Potok, Tempel, *Helv. Chim. Acta* **3**, 794 (1920) (15) Willstaedt, *Ber.* **64**, 2693 (1931). (16) Shoppee, *J. Chem.*
on, Earl,
T 91-93
atsh. **72**,
Matuzov,
J. Gen. Chem (U.S.S.R.) **14**, 120–127 (1944); *C.A.* **39**, 916 (1945). (25) Graymore, Davies, *J. Chem. Soc.* **1945**, 293–294. (26) Vogelsang, *Rec. trav. chim.* **62**, 5–11 (1943); *C.A.* **39**, 1394 (1945).

3:6490 ISOAMYL TRICHLOROACETATE $C_7H_{11}O_2Cl_3$ Beil. II - 209

iso-$C_5H_{11}O.CO.CCl_3$ II_1-(94) II_2-(200)

B.P. 217° (1) D_4^{20} = **1.2314** (2) cf. (3) n_D^{20} = **1.4521** (2)

3:6490 (1) Clermont, *Bull. soc. chim* (2) **40**, 302 (1883). (2) Schjanberg, *Z. physik. Chem.* **A-172**, 229 (1935). (3) Livingston, Morgan, Kramer, *J. Am. Chem. Soc.* **35**, 1836 (1913).

CHAPTER XV

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 1. D_4^{20} greater than 1.1500

(3:6500–3:6999)

3:6500 GLUTARYL (DI)CHLORIDE $C_5H_6O_2Cl_2$ Beil. II - 634, II_1-(273), II_2-(566)

$$\underset{\displaystyle Cl}{\overset{}{O{=}C}}{-}CH_2.CH_2.CH_2{-}\underset{\displaystyle Cl}{C{=}O}$$

B.P.

216–218° cor. (1)		$D_4^{21.5} = 1.3221$ (2)	
107–108° at 16 mm. (2)			
100° at 15 mm. (3)		$D_4^{20} = 1.324$ (2)	$n^{20.2} = 1.47281$ (2)

[For prepn. of $\bar{C}$ from glutaric acid (1:0440) with PCl_5 (1) (2) (3) or with $SOCl_2$ (80–85% yield (4)) (5) see indic. refs.]

Note that $\bar{C}$ may react in either *sym.* or *unsym.* form (6).

[$\bar{C}$ with $AlCl_3$ + C_6H_6 yields (7) (4) 1,5-diphenylpentanedione-1,5 (1,3-dibenzoylpropane) [Beil. VII-775, VII_1-(403)], m.p. 62–63° (7) (4); $\bar{C}$ with $AlCl_3$ + *m*-xylene gives (8) 1,5-di-*m*-xylylpentanedione-1,5, m.p. 60° (8), + γ-(*m*-xyloyl)-*n*-butyric acid, m.p. 118° (8); $\bar{C}$ with $AlCl_3$ + mesitylene gives (72% yield (5)) 1,5-dimesitylpentanedione-1,5, m.p. 133–134° (5).]

$\bar{C}$ on hydrolysis yields glutaric acid (1:0440), m.p. 98° (for the diamide, dianilide, di-*p*-toluidide, and other derivs. corresp. to $\bar{C}$ see 1:0440).

3:6500 (1) Reboul, *Ann. chim.* (5) **14**, 504 (1878). (2) von Auwers, Schmidt, *Ber.* **46**, 479 (1913). (3) Meerburg, *Rec. trav. chim.* **18**, 373 (1899). (4) Skraup, Guggenheimer, *Ber.* **58**, 2493 (1925). (5) Kao, *J. Chinese Chem. Soc.* **3**, 56–59 (1935). (6) Plant, Tomlinson, *J. Chem. Soc.* **1935**, 856. (7) Auger, *Ann. chim.* (6) **22**, 358 (1891). (8) Borsche, *Ber.* **52**, 2080 (1919).

3:6510 β-CHLOROETHYL TRICHLOROACETATE $C_4H_4O_2Cl_4$ Beil. II - 209, II_1—, II_2—

$ClCH_2.CH_2.O.CO.CCl_3$

B.P.

217° at 766 mm. (1)	$D_4^{20} = 1.5357$ (1), cf. (4)	
99.5–100.0° at 14 mm. (2)		$n_D^{20} = 1.48133$ (1) cf. (4)
95–96° at 11 mm. (3)		
68–69° at 1.6 mm. (4)		

[For prepn. (45% yield (3)) from ethylene chlorohydrin (3:5552) + trichloroacetyl chloride (3:5420) + pyridine in ether see (3) (1); for prepn. (70% yield (3)) from β-hydroxyethyl trichloroacetate (3:9099) + $SOCl_2$ see (3).]

$\bar{C}$ on shaking with aq. is smoothly saponified to β-chloroethanol (3:5552) + trichloroacetic ac. (3:1150), no chloride ion being formed (3).

3:6510 (1) Delacre, *Bull. soc. chim.* (2) **48**, 708 (1887). (2) Palomaa, Salmi, Korte, *Ber.* **72**, 797 (1939). (3) Meerwein, Sönke, *Ber.* **64**, 2380 (1931). (4) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 309 (1933).

3:6517 β-CHLORO-β'-HYDROXY-ISOPROPYL ACETATE $C_5H_9O_3Cl$ Beil. II - 142
(Glycerol α-chlorohydrin β-acetate;
β-aceto-α-chlorohydrin;
γ-chloropropylene glycol β-acetate)

CH_2Cl
H—C—O.CO.CH_3
CH_2OH

II_1-(67)
II_2—

B.P. 218° (1) at 760 mm. (2)
108° at 12 mm. (3)

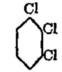
[*See also glycerol α-chlorohydrin α'-acetate* (3:6775).]

[For formn. of $\bar{C}$ from 3-hydroxy-1,2-epoxypropane (glycidol) with AcCl (3:7065) (γ-hydroxy-β-chloro-n-propyl acetate is also formed) see (1); from epichlorohydrin (3:5358) with AcOH in s.t. at 180° see (1); from glycerol α,β-diacetate with PCl_5 see (3).]

Note that the homogeneity of all reported prepns. of $\bar{C}$ is probably open to serious question.

3:6517 (1) Bigot, *Ann. chim.* (6) **22**, 489–491 (1891). (2) Gibson, *J. Soc. Chem. Ind.* **50**, 950 (1931). (3) Wegscheider, Zmerzlikar, *Monatsh.* **34**, 1079–1080 (1913).

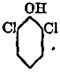
—— **1,2,3-TRICHLOROBENZENE** $C_6H_3Cl_3$ **Beil. V - 203**
V_1-(112)
V_2-(156)



B.P. 218–219° **M.P. 53–54°**

See 3:0990. *Division A: Solids.*

—— **2,6-DICHLOROPHENOL** $C_6H_4OCl_2$ **Beil. VI - 190**
VI_1-(103)
VI_2-(179)



B.P. 219–220° at 740 mm. **M.P. 67°**

See 3:1595. *Division A: Solids.*

3:6525 1,1,2,2,3,3-HEXACHLOROPROPANE $C_3H_2Cl_6$ **Beil. I - 107**
(*sym.*-Hexachloropropane)

Cl
Cl_2CH—C—$CHCl_2$
Cl

I_1-(35)
I_2—

B.P. 218.5° (1) D_4^{34} = **1.7131** (1) n_D^{18} = **1.5262** (1)

[For prepn. of $\bar{C}$ from 1,2,3,3-tetrachloropropene-1 (3:5920) + Cl_2 in sunlight at −30° see (1).] [The product obtd. by (4) from *sym.*-tetrachloroacetone (3:6050) + PCl_5 was probably very impure $\bar{C}$.]

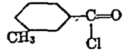
C̄ with alc. KOH loses HCl quant. yielding 1,1,2,3,3-pentachloropropene-1 (3:6075), b.p. 183° (1).

[For use as solvent for cellulose esters see (2) (3).]

(2) Spicers, Ltd. & Hands, Brit. 279,139, (3) Spicers, Ltd. & Hands, French 625,165, *Ann.* 252, 335–338 (1889).

3:6535 *m*-TOLUYL CHLORIDE (*m*-Methylbenzoyl chloride)

C_8H_7OCl Beil. IX - 477, IX_1-(190)



B.P.		M.P.	
219–220°	at 773 mm. (1)	−25° (4)	$D_4^{20} = 1.173$ (3)
218.7–219.7°	at 760 mm. (2)	−23° (1)	
218°	at 724 mm. (1)		
120°	at 38 mm. (3)		
119–120°	at 36 mm. (4)		
[136–138°	at 31 mm. (5)]		
105°	at 20 mm. (6)		
109°	at 15 mm. (7)		
109°	at 8 mm. (8)		
71.2°	at 4 mm. (9)		

[For prepn. of C̄ from *m*-toluic acid (1:0705) with PCl_5 (83% yield (1)) (2) (10), with PCl_5 in $CHCl_3$ (70% yield (3)) (5), with PCl_3 (8), with $SOCl_2$ (95% yield (11)) (12) (6) (9), or with $POCl_3$ + NaCl (or KCl) (13) see indic. refs.; for formn. of C̄ from heptadiyne-1,6-carboxylic acid-4 (*pseudo-m*-toluic acid) with PCl_5 see (14).]

C̄ with pyridine and excess $K_2S_2O_5$ yields (15) *m*-toluic anhydride, m.p. 70–71°.

[For reactn. of C̄ with $AlCl_3$ and various hydrocarbons to yield corresp. ketones, e.g., with C_6H_6 yielding (10) phenyl *m*-tolyl ketone [Beil. VII-440, VII_1-(235)], with toluene yielding (16) *m*-tolyl *p*-tolyl ketone [Beil. VII-451], with *m*-xylene yielding (17) *m*-tolyl ... with $AlCl_3$ alone at 130–140° ... Beil. VII-815], m.p. 236°.]

... ₂ (20) gives (yield: 83% (20), 43% (19)) *m*-methylacetophenone (1:5527), b.p. 220°.]

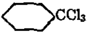
[C̄ with Cl_2 at 160–180° gives (90% yield (21)) (6) *m*-(chloromethyl)benzoyl chloride (ω-chloro-*m*-toluyl chloride), b.p. 149–150° at 20 mm. (21); C̄ with Br_2 at 185–195° gives (50% yield (22)) ω-bromo-*m*-toluyl bromide, b.p. 167° at 22 mm. (22).]

[C̄ with MeOH yields methyl *m*-toluate (1:3781), b.p. 221°; C̄ with EtOH yields ethyl *m*-toluate (1:3942), b.p. 234°; for study of rate of reactn. see (4).]

C̄ on hydrolysis yields *m*-toluic acid (1:0705), m.p. 110–111° (for study of rate see (23)). —For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *m*-toluic acid (1:0705).

3:6535 (1) van Scherpenzeel, *Rec. trav. chim.* 20, 162 (1901). (2) Kohlrausch, Pongratz, Stockmair, ... (4) Norris, Young, *J. Am.* ... 910). (6) Morgan ... 94 (1899). (8) Fra... *m. Chem. Soc.* 58, ... (11) ... Shopee,

J. Chem. Soc. **1932**, 700. (13) Kissling (to I G.), Ger. 642,519, March 10, 1937; *Cent.* **1937**, I, 3874; *C.A.* **31**, 5816 (1937). (14) Perkin, Simonsen, *J. Chem. Soc.* **91**, 847 (1907). (15) Gasopoulos, *Praktika Akad. Athenon* **6**, 347–353 (1931); *Cent* **1932**, I 3171. (16) Scharwin, Schorygin, *Ber* **36**, 2027 (1903). (17) Morgan, Coulson, *J. Chem. Soc.* **1929**, 2213. (18) Seer, *Monatsh.* **32**, 154–157 (1911). (19) Mauthner, *J. prakt. Chem.* (2) **103**, 394 (1921/22). (20) Gilman, Nelson, *Rec. trav chim.* **55**, 528–530 (1936).
(21) Titley, *J. Chem. Soc.* **1928**, 2582. (22) Davies, Perkin, *J. Chem. Soc.* **121**, 2210 (1922). (23) Berger, Olivier, *Rec. trav. chim.* **46**, 524–527 (1927).

3:6540 BENZOTRICHLORIDE (Phenylchloroform, ω,ω,ω-trichlorotoluene)  $C_7H_5Cl_3$ Beil. **V - 300**, **V$_1$-(152)**, **V$_2$-(233)**

B.P.			F.P.			
220.5–221.5°		(1)	**−4.4°**	(8)	D_4^{20} = **1.3741**	(8)
220.9°		(2)	**−4.75°**	(3)	**1.37563**	(4)
220.7°	at 761 mm.	(3)	**−5.0°**	(9) (10)	n_D^{20} = **1.55789**	(8)
214–216°		(4)	**−8.1°**	(7)	**1.5579**	(4)
213.0–213.5°		(5)			**1.55726**	(11)
129°	at 60 mm.	(6)			D_-^{15} = **1.3775**	(3)
105°	at 25 mm.	(7)				
110.7°	at 23 mm.	(3)				
89.0–89.5°	at 10 mm.	(8)				

Colorless liquid insol. aq., sol. many org. solvents. — Ord. samples of $\bar{C}$ may also cont. benzal (di)chloride (3:6327) or even benzyl chloride (3:8535). — $\bar{C}$ when pure is stable in dry air, but ord. material (contg. dislvd. HCl) hydrolyzes rapidly in moist air (3). — The very high value (93) of molal f.p. lowering of $\bar{C}$ prob. accounts for difficulty of earlier workers in attaining high f.p. values (3). — For removal of dislvd. HCl from $\bar{C}$ by treat. with $PbCO_3$ see (9). — For purification of $\bar{C}$ via crystallization see (10); for comml. purification see (12).

$\bar{C}$ forms const.-boilg. mixts. with various cpds., e.g., $\bar{C}$ with *p*-dibromobenzene (b.p. 220.25°) forms an azeotrope, b.p. 219.6° at 760 mm., contg 28 wt. % $\bar{C}$ (2); $\bar{C}$ with nitrobenzene (b.p. 210.75°) forms an azeotrope, b.p. 210.72° at 760 mm., contg. 1.5 wt. % $\bar{C}$ (2); $\bar{C}$ with *o*-nitrotoluene (b p. 221.85°) forms an azeotrope, b.p. 219.55° at 760 mm., contg. 75.5 wt. % $\bar{C}$ (13); $\bar{C}$ with methyl salicylate (1:1750) (b.p. 222.35°) forms an azeotrope, b.p. 220.75° at 760 mm., contg. 97 wt. % $\bar{C}$ (13).

$\bar{C}$ is impt. intermediate in prepn. of benzoic acid (see below under hydrolysis), in prepn. of certain dyestuffs (see below), and in prepn. of acyl halides and anhydrides (see below); for use in prepn. of films of cellulose ethers see (14).

[For prepn. of $\bar{C}$ from toluene with Cl_2 especially in pres. of light and/or other catalysts see (15) (16) (17) (18); with Cl_2 in pres. of PCl_3 (3) cf. (19); with $SOCl_2$ in s.t. at 220° for 18 hrs. (20) or at 230–250° (21) see indic. refs.; with NOCl at 350° see (22); for formn. of $\bar{C}$ from benzal (di)chloride (3:6327) with Cl_2 (23) or with NOCl at 150° (24) see indic. refs.; from benzyl chloride (3:8535) by htg. with $PbCl_4.2NH_4Cl$ see (25); from benzoyl chloride (3:6240) with PCl_5 see (26); from benzotrifluoride + acetyl chloride + $AlCl_3$ as directed see (8); from benzyl ethers with PCl_5 see (27).]

[$\bar{C}$ on reductn. in alc. soln. with H_2 in pres. of colloidal Pd (28) or $Pd/CaCO_3$ (29) reacts bimolecularly giving (75% yield (28)) tolane tetrachloride (diphenylacetylene tetrachloride) (3:4496), colorless cryst. from AcOH, m.p. 162–163° (28), also obtd. from $\bar{C}$ by other treatments (see below); this prod. with H_2 + $Pd/CaCO_3$ in alc. KOH is further reduced yielding (29) dibenzyl (1:7149) (use in quant. detn. of its halogen (29)). — $\bar{C}$ with hydra-

zinc hydrate in MeOH/KOH in pres. of $Pd/CaCO_3$ refluxed for 1½ hrs. gives (42% yield (30)) a mixt. of the two geom. isomeric tolane dichlorides consisting mainly of the α-isomer (3:4210), colorless tbls. from alc., m.p. 148° (30), with a little of the β-isomer (3:1380), m.p. 61° (30); despite their unsaturation these prods. reduce further only with difficulty.

[C̄ satd. with Cl_2 and stood in sunlight for 8 months or C̄ with liq. Cl_2 in sunlight for a few days adds 3 Cl_2 yielding (31) 1,2,3,4,5,6-hexachloro-1(trichloromethyl)cyclohexane, cryst. from $CHCl_3$ or by sublimation, m.p. 103° (31); this may be accompanied by a little pentachlorotrichloromethylcyclohexene, m.p. 132–134° (31). — C̄ with Cl_2 in pres. of I_2 yields (32) a mixt. of mono- and di-chlorobenzotrichlorides.]

[C̄ on pyrogenic decompn. over Pt at red heat yields (32*a*) cf. (34) tolane tetrachloride (3:4496) together with its isomorphous mixt. with α-tolane dichloride (see above). — C̄ with Na in liq. NH_3 yields (33) 5% dibenzyl (1:7149) accompanied by much nitrogenous tar. — C̄ with Zn in ether soln. reacts vigorously yielding (35) a deep green soln. contg. tolane dichloride (see above). — C̄ with equal wt. reduced Cu at 100° for 10 hrs. yields (36) tolane tetrachloride, m.p. 162° (3:4496); note that distn. of crude reactn. prod. leads to further reactn. and formation (36) (37) of α- and β-tolane dichlorides (see above). — C̄ with C_6H_6 in pres. of powdered chromium metal at 100° for 5 hrs. gives (17% yield (38)) triphenylchloromethane (3:3410), m.p. 106° (38). — C̄ with small proportion of $AlCl_3$ (0.1 mole) at 50–60° evolves HCl and gives a mixt. (39) contg. 40% α,α-dichloro-*m*-trichloromethyl-diphenylmethane, m.p. 59–61°, + 10% *m*-(α',α'-dichloro-*m*'-trichloromethylbenzyl)-α,α-dichlorodiphenylmethane, oil, + 34% unchanged C̄. — C̄ with $AlCl_3$ in C_6H_6 (39) or C̄ with Al + $HgCl_2$ in C_6H_6 (40) gives (62% yield (39)) 9,9',10,10'-tetraphenyl-9,10-dihydroanthracene, cryst. from acetone or lgr., m.p. 159° (40), 157–158° (39).]

[C̄ with MeMgCl in ether gives two types of reactn. according to concn. (41); e.g., C̄ with dilute MeMgCl yields tolane tetrachloride (3:4496) + ethane + $MgCl_2$, while C̄ with conc. MeMgCl gives in 22% yield a mixt. of the two geom. isomers of tolane dichloride (see above) consisting of 5 pts. of the *trans* form (3:4210), m.p. 138–139° (41), together with 1 pt. of the *cis* form (3:1380), m.p. 63° (41), separable by fractional crystn. from alc. — For reactn. of C̄ with EtMgBr see (42). — C̄ does *not* (43) react with excess mercury di-*p*-tolyl.]

[C̄ with HF gas in Cu flask at 0° for 72 hrs. (44), or C̄ with SbF_3 (45) (46), or C̄ with $SbF_3.2NaF$ at 130–140° (47), gives (yields: 75–95% (44), 75% (45), benzotrifluoride, b.p. 102.3°, m.p. −29°. — Note that C̄ with ZnF_2 in Cu flask at 120° for 6 hrs. gives (65% yield (57)) benzoyl fluoride, b.p. 155–156° (57), also that C̄ + KF in HCOOH gives (16% yield (68)) formyl fluoride, b.p. −26° at 750 mm. (68).]

C̄ on complete hydrolysis yields benzoic acid (1:0715): e.g., C̄ on htg. with anhydrous HCOOH yields (48) BzOH + CO + HCl (use in detn. of side-chain halogen (49)); C̄ with aq. in s.t. at 150° (15) or with aq. at 90–95° in pres. of Fe salts (50), or with aq. vapor at 550–850° over cat. (51), or with aq. + $ZnCl_2$ at 110–115° under press. (52), or with aq. $CaCO_3$ at 90° followed by acidif. with minl. acid (53) yields BzOH; note, however, although C̄ in ether soln. is only slowly hydrolyzed by aq. at room temp. (54) yet C̄ adequately shaken with aq. at room temp. is completely hydrolyzed (use in detn. of C̄ + benzal (di-)chloride + benzyl chloride by titration with std. alk. using thymolsulfonphthalein (55)) and C̄ if subjected to actn. of steam (as in steam distn. of mixt. with volatile cpds.) is partially hydrolyzed (8). — [For study of kinetics of hydrolysis of C̄ in aq. acetone at 30° in pres. of acids, bases, or salts see (1).]

[C̄ on partial hydrolysis yields benzoyl chloride (3:6240): e.g., C̄ with limited amt. aq. in pres. of H_2SO_4 or $FeCl_3$ (56), or C̄ with ord. comml. $ZnCl_2$ at 120° (57) (58), or C̄ with aq. vapor over tin phosphate at 240° (59), or C̄ with pure ZnO at 100° (57), or C̄ with benzoic

acid in boilg. nitrobenzene (60), yields BzCl; note, however, that C̄ with *pure* $ZnCl_2$ fails to react but addn. of 1 mole aq. or initial use of tech. $ZnCl_2$ gives BzCl (57).]

[C̄ htd. with carboxylic acids or anhydrides especially in pres. of $ZnCl_2$ is often used to prepare a mixture of benzoyl chloride with the acid chloride of the acid employed, particularly in cases where the two acyl chlorides are readily separable: e.g., C̄ with phthalic anhydride (1:0725) (61) (62) or phthalic acid (1:0820) (62) + $ZnCl_2$ at 110–120° or above gives 96% yield BzCl (3.6240) + 93% *sym.*-phthalyl (di)chloride (3:6900); for other examples see under chloroacetyl chloride (3:5235), dichloroacetyl chloride (3:5290), trichloroacetyl chloride (3:5420), fumaryl (di)chloride (3:5875), and terephthalyl (di)-chloride (3:2205). — Similarly C̄ with salts of sulfonic acids yields BzCl + the corresp. sulfonyl chloride: e g., C̄ + sodium β-naphthalenesulfonate gives (63) 90% yield BzCl + 80% yield β-naphthalenesulfonyl chloride.]

[C̄ under certain conditions may be converted to benzoic anhydride (1:0595): e.g., C̄ with BzOH + trace Fe salts htd. 6 hrs. at 110–115° under reflux (64), or C̄ with NaOBz (65), or C̄ with ord. conc H_2SO_4 (66), or C̄ in AcOH in pres. of phosgene (67), yields Bz_2O.]

C̄ very readily undergoes alcoholysis: e.g., C̄ with EtOH in pres. of $ZnCl_2$ yields (69) ethyl benzoate (1.3721); note, however, that C̄ + abs. EtOH in s.t. at 130–140° (70) or C̄ + trace sublimed $FeCl_3$ treated at 80–110° with 95% alc. (71) yields benzoyl chloride (3:6240) + ethyl chloride (3·7015); furthermore that C̄ + ethyl acetate (2 moles) in pres. of $ZnCl_2$ yields (69) ethyl benzoate (1:3721) + acetyl chloride (3:7065) + ethyl chloride (3.7015).

C̄ reacts with phenols to give various products according to circumstances: C̄ with aq. (72) (74) or better alc. (73) sodium phenolate (3 moles) gives at 100° small yields of phenyl benzoate (1:2257), m.p. 71°, and of *o*-hydroxybenzophenone (1:1414), m.p. 41°, together with other prods. notably benzaurin (see below). — C̄ with phenol in pres. of ZnO gives (75) phenyl benzoate (see above) + *p*-hydroxybenzophenone (1:1560), m.p. 134°. — C̄ with phenol (2 moles) htd. at 100° and reactn. prod. treated with steam yields (76) (77) 4,4′-dihydroxytriphenylcarbinol (=phenolbenzein=4′-hydroxyfuchsone=benzaurin) [Beil. VI-1145, $VIII_1$-(589)], as red crystn. powder (diacetate, m.p. 119° (76) (77); dibenzoate, m p. 183–184° (76)), accompanied by *p*-hydroxybenzophenone (see above). — [For corresp. reactns. of C̄ with *o*-cresol (1:1400) yielding *o*-cresolbenzein (78) (79), with thymol (1:1430) yielding thymolbenzein (80), with resorcinol (1:1530) yielding resorcinolbenzein (76), or with pyrogallol (1:1555) yielding pyrogallolbenzein (81) see indic. refs. — For reactn. of C̄ with α-naphthol (1:1500) (73) (94) (95) (or with 1-hydroxynaphthoic acid-2 (82) (83) (95)) yielding 4-(1-hydroxynaphthyl) phenyl ketone (or the corresp. 4-(1-hydroxy-2-carboxynaphthyl) phenyl ketones) respectively *see indic. refs.; for reactn. of* C̄ *with* β-naphthol (1:1540) see (84).]

C̄ with ammonia or amines gives varied reactns. — C̄ with liq. NH_3 (85) or with NH_4Cl in s.t. at 200° (86) gives (75% yield (85)) benzonitrile; C̄ with conc. aq. NH_4OH in s.t. at 130° yields (85) benzoic acid + benzamide + benzonitrile. — C̄ (1 mole) with aniline (2 moles) warmed together without solvent or with $ZnCl_2$ in AcOH soln. gives (87) *N,N′*-diphenylbenzamidine hydrochloride [Beil. XII-273, XII_1-(202)], the free base of which has m.p. 147°; note, however, that C̄ with aniline hydrochloride + nitrobenzene + Fe filings htd. at 180° for 3–4 hrs. yields (87) the dyestuff Doebner's Violet (the HCl reactn. prod. of 4,4′-diaminotriphenylcarbinol) [Beil. XIII-742, $XIII_1$-(293)]. — C̄ (1 mole) with dimethylaniline (2 moles) htd. at 100° preferably in pres. of $ZnCl_2$ yields (86) the dyestuff Malachite Green (the HCl reactn. prod. of 4,4′-dimethylaminotriphenylcarbinol) [Beil. XIII-743, $XIII_1$-(293)] (see Ⓟ below); analogous dyestuffs from other tertiary amines cannot be discussed here.

[C̄ with excess phenylhydrazine in alc. does not react until Cu powder is added; the

solution then (89) rapidly turns or.-red. and on cooling soon ppts. a mixture of benzaldehydephenylhydrazone, m.p. 157° (see 1:0195) (doubtless accounted for by reductn. of C̄ to benzal (di)chloride (3:6327) at the expense of phenylhydrazine), together with phenylhydrazine hydrochloride. — C̄ + excess phenylhydrazine heated in alc. without Cu (89) turns dark red and ppts. a mixt. of "formazylbenzene" [Beil. XVI-17], red lfts. from alc., m.p. 173° (doubtless accounted for as above), and phenylhydrazine hydrochloride.]

[C̄ with amides or ammonium salts gives on htg. mixtures of corresp. nitriles and acid halides: e.g., C̄ with benzamide at 140° yields (90) benzonitrile + benzoyl chloride; C̄ with *p*-toluamide at 140° yields (90) benzonitrile, *p*-tolunitrile, benzoyl chloride, and *p*-toluyl chloride (3:6600). — For patents exemplifying this type of reactn. see (91) (92).]

C̄ on mononitration, e.g., with 0.44 pt. fumg. HNO_3 + 0.44 pt. conc. H_2SO_4 at 25–30° for ½ hr. (4), gives 85% yield *m*-nitrobenzoic acid, m.p. 140° (4); very possibly hydrolysis here precedes nitration since C̄ on nitration with N_2O_5 in cold CCl_4 gives (32) (93) an oily mixt. of nitrobenzotrichlorides more stable to hydrolysis than original C̄, but which on cleavage with alk. or conc. H_2SO_4 yields a mixt. of nitrobenzoic acids containing 70% *m*-nitrobenzoic acid (for other studies of nitration of C̄ see (5) (10)). — C̄ on dinitration by soln. in 5.4 pts. conc. H_2SO_4 and treatment with 6.8 pts. fumg. HNO_3 at 185° for 1 hr. gives (4) 33% yield of 3,5-dinitrobenzoic acid, m.p. 203–204° (4).

[C̄ cannot be sulfonated without hydrolysis of the $—CCl_3$ group; C̄ with conc. H_2SO_4 even at 30° yields (66) benzoic acid (or its anhydride). — However, C̄ with gaseous SO_3 at room temp. (6) gives on subsequent vac. distn. an oil (perhaps *m*-sulfobenzotrichloride) which with aq. yields *m*-sulfobenzoic acid [Beil. XI-384, XI_1-(98)], dihydrate, m.p. 97–98°, losing aq. at 160° yielding anhydrous acid, m.p. 140–141° (6).]

Ⓟ **Malachite Green formation.** C̄ (1 drop) + dimethylaniline (1 drop) warmed with 0.1 g. fused $ZnCl_2$ gives intense green color.

Ⓓ **Benzoic acid:** C̄ on refluxing with *aq.* NaOH soln., subsequently acidified, ppts. benzoic acid (1:0715), m.p. 121°.

3:6540 (1) Olivier, Weber, *Rec. trav. chim.* **53**, 881, 884 (1934). (2) Lecat, *Rec. trav. chim.* **47**, 14, 17 (1928). (3) Swarts, *Bull. soc. chim. Belg.* **31**, 375–377 (1922). (4) Sah, Lei, Wang, *Sci. Repts. Natl. Tsinghua Univ.* **A-2**, 137–
Flurscheim, Holmes, *J. Chem. Soc.* 1[illegible]
258 (1935); (2) **143**, 127–138 (1935).
Cent. **1914**, I 618. (8) Henne, Newm[illegible]
Roy. Soc. London **A-133**, 673 (1931).
(1914).

(11) Dummer, *Z. anorg. allgem. Chem.* **101**, 37 (1920). (12) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; *Cent.* **1931**, II 497. (13) Lecat, *Ann. Soc. sci. Bruxelles* **48**, I [illegible]

272, 160 (1892). (20) Pollak, Rudich, *Monatsh.* **43**, 218 (1922).

(21) Meyer, *Monatsh.* **36**, 729 (1915). (22) Moyer (to Solvay Process Co.), U.S. 2,152,357, March 3, 1939; *Cent.* **1939**, II 1775; *C.A.* **33**, 5001 (1939). (23) Limpricht, *Ann.* **139**, 321–325 (1866). (24) Perrot, *Compt. rend.* **198**, 1425 (1934). (25) Seyewetz, Trawitz, *Compt. rend.* **136**, 241 (1903). (26) Limpricht, *Ann.* **134**, 55–57 (1865). (27) Whitmore, Langlois, *J. Am. Chem. Soc.* **55**, 1518 (1933). (28) Borshce, Heimburger, *Ber.* **48**, 458 (1915). (29) Busch, Stöve, *Ber.* **49**, 1067–1068 (1916). (30) Busch, Weber, *J. prakt. Chem.* (2) **46**, 12–13, 50–52 (1936).
(3 [illegible] 315–319
(191 [illegible] . **52**,
2825 [illegible] Clar,
Czal [illegible] *r.* **15**,
898– [illegible] Vohl,
Wer [illegible]

(41) Fuson, Ross, *J. Am. Chem. Soc.* **55**, 720–723 (1933). (42) Sanna, *Cent.* **1937**, II 2345. (43) Whitmore, Thurman, *J. Am. Chem. Soc.* **51**, 1497 (1929). (44) Simons, Lewis, *J. Am.*
6) Booth, Elsey,
March 1, 1937;
(49) Gavankar,
(1938).
orge (to
kelbach
Straus,
Hüssy, *Ber.* **42**, 2180–2181 (1909). (55) Lubs, Clark, *J. Am. Chem. Soc.* **40**, 1449–1453 (1918).
(57) Davies, Dick, *J. Chem. Soc.*
U S. 1,557,154, Oct. 13, 1925;
(*Moscow*) **1934**, No. 1, 30–34;
3, 1934; *C.A.* **29**, 2973 (1935).
(60) British Dyestuff Corp & Bunberg & Shepherdson, Brit. 293,924, Aug. 9, 1928; *Cent.* **1929**, I 1614.

165,747, Aug. 24, 1921, *Cent.* **1922**, II 1218. (66) Jenssen, *Ber.* **12**, 1495 (1879); Ger. 6,685, Oct. 30, 1878. (67) Béhal, *Compt. rend.* **148**, 648 (1909). (68) Nesmeyanov, Kahn, *Ber.* **67**, 370–373 (1934). (69) Jacobsen, Ger. 11,494; *Friedländer* **1**, 24. (70) Limpricht, *Ann.* **135**, 87 (1865).

(71) Verein chem metallurg. Prod , Ger. 472,422, Feb. 28, 1929; *Cent.* **1929**, I 2823. (72) Heiber, *Ber.* **24**, 3684–3687 (1891). (73) Sen, Ray, *J. Indian Chem. Soc.* **9**, 181–183 (1932). (74) Hamada, *Science Repts. Tohoku Imp. Univ., First Ser.* **22**, 55–60 (1933); *Cent.* **1933**, II 871; *C.A.* **27**, 3928 (1933). (75) Doebner, Stackmann, *Ber* **9**, 1918–1920 (1876). (76) Meyer,

Dilthey, Quint, Heinen, *J. prakt. Chem.* (2) **152**, 66–68 (1939). (85) Franklin, *J. Am. Chem. Soc.* **55**, 4915 (1933). (86) Fireman, *J. Am. Chem. Soc* **52**, 2951–2954 (1930). (87) Doebner, *Ann* **217**, 239–249 (1883). (88) Doebner, *Ann.* **217**, 250–261 (1883). (89) Bodforss, *Ber.* **59**, 670 (1926). (90) Titherly, Holden, *J. Chem. Soc.* **101**, 1881–1889 (1912).

(91) I G , Brit. 323,948, Feb. 6, 1930; *Cent.* **1930**, I 2630. (92) Hopff (to I.G.), Ger. 517,760,

II 614–615.

U.S. 1,713,101, May 14, 1929; *Cent.* **1929**, II 1215; *C.A.* **23**, 3234 (1929). (6) Swarts, *Bull. soc. chim.* (3) **13**, 992 (1895). (7) I.G., French 703,816, May 6, 1931; *Cent.* **1931**, II 1317.

3:6582 DIMETHYL CHLOROFUMARATE $C_6H_7O_4Cl$ Beil. II - 744, II_1-(302), II_2-(640)

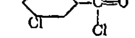
Cl—C—COOCH$_3$
‖
CH$_3$OOC—CH

B.P.					
224° (1)	$D^{25}_{4\,vac.}$ = 1.2809 (2)				
115.5° cor. at 18 mm. (2)	D^{20}_{4} = 1.300 (3)	n^{20}_{He} = 1.471 (3)			
108° at 15 mm. (3)	$D^{17.0}_{4}$ = 1.3028 (3)	$n^{17.0}_{He}$ = 1.47198 (3)			

[For prepn. of Č from chlorofumaric acid (3:4853) in abs. MeOH with HCl gas (1) or conc. H_2SO_4 (3) see indic. refs.; from chlorofumaryl (di)chloride (3:6105) with MeOH under reflux see (1).]

3:6582 (1) Kauder, *J. prakt. Chem.* (2) **31**, 26–28, 32 (1885). (2) Walden, Swinne, *Z. physik. Chem.* **79**, 741 (1912). (3) von Auwers, Harres, *Ber.* **62**, 1679, 1686–1687 (1929).

3:6590 *m*-CHLOROBENZOYL CHLORIDE $C_7H_4OCl_2$ Beil. IX - 338, IX_1-(130)



B.P.				
225° (1) (2)	143–145°	at	40 mm.	(6)
224.8–228.2° (3)	117.5°	at	26 mm.	(7)
224–227° (4)	112°	at	21 mm.	(7)
222° (5)	109.5°	at	19 mm.	(7)
	103.5°	at	15 mm.	(7)
	110°	at	15 mm.	(8)
	103.4°	at	12.5 mm.	(18)
	99.5°	at	12.5 mm.	(7)
	91.5°	at	10 mm.	(7)
	77.5–78°	at	1 mm.	(9)

[For prepn. of Č from *m*-chlorobenzoic acid (3:4392) with PCl_5 (76% yield (8)) (1) (5) or with $SOCl_2$ (10) (6) see indic. refs.; from benzoyl chloride (3:6240) with $Cl_2 + FeCl_3$ (83.5% Č) see (7) (11); from tetrahydroxybenzoic acid [Beil. X-535, X_1-(270)] with 5 moles PCl_5 see (12); from *o*-sulfobenzoic acid with 2 moles PCl_5 see (1) (13).]

[Note that for the isomeric *p*-chlorobenzoyl chloride (3:6550) htg. with P_2O_5 in toluene yields (16) the corresp. anhydrides; although this reactn. is not recorded for Č yet the corresp. *m*-chlorobenzoic acid anhydride, ndls. from alc. (17) or from lt. pet. (16), m.p. 95.5° (16), 95° (17), has been obtd. from *m*-chlorobenzoic acid (3:4392) with P_2O_5 in boilg. toluene (30% yield (16)) or with oxalyl dichloride (3:5060) in boilg. C_6H_6 (17).]

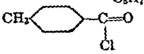
[Č with MeOH yields (5) methyl *m*-chlorobenzoate (3:6670), b.p. 231°; Č with EtOH yields (1) ethyl *m*-chlorobenzoate (3:6770), b.p. 245°.] [For studies of rate of alcoholysis of Č see (14) (9).]

[Č with $C_6H_6 + AlCl_3$ gives (65% yield (6)) (2) (4) *m*-chlorobenzophenone (3:2160), m.p. 82–83°; Č with naphthalene + $AlCl_3$ in CS_2 gives (73% yield (15)) *m*-chlorophenyl α-naphthyl ketone, pale yel. pr. from alc., m.p. 77–79° (15).]

Č on hydrolysis (e.g., by boilg. with aq. (7)) yields *m*-chlorobenzoic acid (3:4392). — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to Č see *m*-chlorobenzoic acid (3:4392).

3:6590 (1) Limpricht, von Uslar, *Ann.* **102**, 262–263 (1857). (2) Hantzsch, *Ber.* **24**, 57 (1891). (3) Kohlrausch, Pongratz, Stockmair, *Monatsh.* **67**, 108 (1935). (4) Norris, Blake, *J. Am. Chem. Soc.* **50**, 1812. (5) Montagne, *Rec. trav. chim.* **19**, 55, 58 (1900). (6) Bergmann, Bondi, *Ber.* **64**, 1477 (1931). (7) Hope, Riley, *J. Chem. Soc.* **121**, 2510–2527 (1922). (8) Novello, Miriam, Sherwin, *J. Biol. Chem.* **67**, 558 (1926). (9) Norris, Young, *J. Am. Chem. Soc.* **57**, 1420–1424 (1935) (10) Frankland, Carter, Adams, *J. Chem. Soc.* **101**, 2470–2477 (1912).
(11) Hope, Riley, *J. Chem. Soc.* **123**, 2470–2480 (1923). (12) Graebe, *Ann.* **138**, 200–202 (1866). (13) Otto, *Ann.* **122**, 156 (1862). (14) Berger, Olivier, *Rec. trav. chim.* **46**, 516–527 (1927). (15) Scholl, Seer, *Ber.* **55**, 113 (1922). (16) Rule, Paterson, *J. Chem. Soc.* **125**, 2161 (1924). (17) Adams, Wirth, French, *J. Am. Chem. Soc.* **40**, 427 (1919). (18) Thompson, Norris, *J. Am. Chem. Soc.* **58**, 1956 (1936).

3:6600 *p*-**TOLUYL CHLORIDE** (*p*-Methylbenzoyl chloride) C_8H_7OCl Beil. IX - 486, IX_1-(193)



B.P.			F.P.		
225.5–226.7°		(1)	−3.9° (5)	D_4^{20} = 1.1686 (5)	n_D^{20} = 1.5449 (5)
225–227°		(2)	−2.0° (6)		
224–226°	at 720 mm.	(3)			
125°	at 36 mm.	(14)			
101–102°	at 16 mm.	(13)			
102°	at 15 mm.	(4)			
102.7°	at 14 mm.	(5)			
95–95.5°	at 10 mm.	(6)			
72.8–73.0°	at 4.5 mm.	(7)			
70–71°	at 4 mm.	(8)			
90–90.5°	at 3 mm.	(9)			

[For prepn. of C̄ from *p*-toluic acid (1:0795) with PCl_5 (100% yield (3)) (6) (10), with PCl_3 (11), with $SOCl_2$ (95% yield (12)) (2) (7) (13) (14), with $POCl_3$ + NaCl (KCl) (15) see indic. refs.]

[C̄ with pyridine and excess $K_2S_2O_5$ yields (16) *p*-toluic anhydride, m.p. 94° (also formed as by-product of prepn. of C̄ with PCl_5 (6)).]

[For reactn. of C̄ with $AlCl_3$ and various hydrocarbons to yield ketones, e.g., with C_6H_6 yielding (3) phenyl *p*-tolyl ketone (1:5160), with toluene yielding (17) di-*p*-tolyl ketone (1:5185), with biphenyl yielding (18) (13) *p*-tolyl *p*′-xenyl ketone, with naphthalene yielding (19) α-naphthyl *p*-tolyl ketone, with *m*-xylene yielding (14) *p*-tolyl *m*-xylyl ketone, with *p*-xylene yielding (14) *p*-tolyl *p*-xylyl ketone, with isopropylbenzene (cumene) yielding (20) *p*-cumyl *p*-tolyl ketone see indic. refs.]

[C̄ with EtZnI yields (21) ethyl *p*-tolyl ketone [Beil. VII-317, VII_1-(170)], b.p. 238°.]

[C̄ with Cl_2 at elevated temp yields (22) *p*-(chloromethyl)benzoyl chloride (ω-chloro-*p*-toluyl chloride, b.p. 150–155° at 22 mm. (22); C̄ with Br_2 at 185–190° yields (23) a mixt. of *p*-(bromomethyl)benzoyl *chloride*, b.p. 155–156° at 20 mm., and *p*-(bromomethyl)benzoyl bromide, b.p. 170–171° at 20 mm., m.p. 56° (23).]

[C̄ with MeOH yields methyl *p*-toluate (1:2071), m.p. 33°, b.p. 222.5°; C̄ with EtOH yields ethyl *p*-toluate (1:3917), b.p. 234.5°; for study of rate of reactn. with MeOH see (24), with EtOH see (9), with isopropyl alc see (25).]

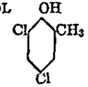
C̄ on hydrolysis yields *p*-toluic acid (1:0795), m.p. 178°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *p*-toluic acid (1:0795).

3:6600 (1) Kohlrausch, Pongratz, Stockmair, *Monatsh.* **67**, 108 (1936). (2) Meyer, *Monatsh.* **22**, 425 (1901). (3) Ador, Rilliet, *Ber.* **12**, 2298–2299 (1879). (4) Frankland, Aston, *J. Chem.*

Soc. **75**, 494 (1899). (5) Martin, Partington, *J. Chem. Soc.* **1936**, 1177. (6) van Scherpenzeel, *Rec. trav. chim.* **20**, 156 (1901). (7) Thompson, Norris, *J. Am. Chem. Soc.* **58**, 1955 (1936).
(9) Norris, Young, *J. Am. Chem. Soc.*
(1896). (12) Maxim, *Bul. Soc. Chim.*
nd. **180**, 1349–1351
eer, *Ann.* **394**, 147
–1689 (1936); *Cent.*
1937, I 2369; *C.A.* **31**, 2591 (1937).

(21) Mauthner, *J. prakt. Chem.* (2) **103**, 294 (1921/22). (22) Badische Anilin- und Soda-Fabrik., Ger. 239,311, Oct. 10, 1911; *Cent.* **1911**, II 1394; Ger. 240,835, Nov. 15, 1911; *Cent.* **1911**, II 1843. (23) Titley, *J. Chem. Soc.* **1928**, 2581. (24) Norris, Fasce, Staud, *J. Am. Chem. Soc.* **57**, 1415–1420 (1935). (25) Norris, Gregory, *J. Am. Chem. Soc.* **50**, 1813–1816 (1928).

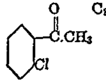
—— **4,6-DICHLORO-2-METHYLPHENOL** $C_7H_6OCl_2$ **Beil. VI - 359**
VI_1-(174)
VI_2-(332)



B.P. 226.5° **M.P. 56°**

See 3:1020. *Division A: Solids.*

3:6615 o-CHLOROACETOPHENONE C_8H_7OCl **Beil. VII —**
(*o*-Chlorophenyl methyl ketone) **VII_1-(151)**



B.P.					
228–229° at 758 mm.	(10)	D_{25}^{25} = 1.1884	(1)	n_D^{25} = 1.685	(1)
227–228° at 738 mm.	(1)	D_4^{20} = 1.198	(4)	n_{He}^{20} = 1.5483	(4)
226–228°	(2)	$D_4^{16.6}$ = 1.2016	(4)		
220–222°	(3)				
113° at 18 mm.	(4)				
98° at 6 mm.	(5)				

Colorless mobile liquid with agreeable odor.

[For prepn. of $\bar{C}$ from *o*-chlorophenyl-methyl-carbinol (4) (5) by oxidn. with CrO_3 see (4) (5); from methyl *o*-chlorobenzoylacetate (60% yield (2)) or from ethyl *o*-chlorobenzoylacetate (80% yield (1)) (54% from $\bar{C}$ (10)) on ketonic hydrol. with boilg. 20% H_2SO_4 for 10–12 hrs. see indic. refs.; from *o*-chlorobenzonitrile [Beil. IX-336] with MeMgI in ether (56% yield) see (3).]

[$\bar{C}$ with CuCN on htg. in mixt. of quinoline + pyridine as directed (6) gives 20% yield *o*-cyanoacetophenone, m.p. 48°, b.p. 148° at 12 mm. (6); for behavior of $\bar{C}$ on htg. with CuCN in quinoline at 210° or with CuCN + phthalonitrile in quinoline yielding copper-contg. pigments of the phthalocyanine type see (7).]

[$\bar{C}$ on htg. with 50% KOH as directed (8) gives small yield *o*-chlorobenzoic acid.]

[$\bar{C}$ on mononitration with 10 pts. HNO_3 (D = 1.52) at 0° gives (85% yield (1)) 2-chloro-4-nitroacetophenone, colorless pr. from alc., m.p. 62° (1) (for condens. of this prod. with arylamines to give substituted acridines see (9)).]

Ⓓ *o*-Chloroacetophenone oxime: ndls. from aq., m.p. 112–113° (4), 103° (1).

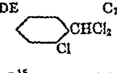
Ⓓ *o*-Chloroacetophenone *p*-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 215° (2). (The phenylhydrazone of C̄ is unstable (2).)

Ⓓ *o*-Chloroacetophenone 2,4-dinitrophenylhydrazone: dark yel. lfts. from AcOEt, m.p. 206° (3).

Ⓓ *o*-Chloroacetophenone semicarbazone: cryst. from MeOH, m.p. 178–179° (3), from 40% AcOH, m.p. 159–160° (2).

3:6615 (1) Thorp, Brunskill, *J. Am. Chem. Soc.* **37**, 1260–1261 (1915). (2) Wahl, Rolland, *Ann chim* (10) **10**, 28–29 (1928). (3) Borsche, Scriba, *Ann.* **541**, 290 (1939). (4) von Auwers, Lechner, Bundesmann, *Ber.* **58**, 49–50 (1925). (5) Ferbwerke Meister Lucius Brüning, Brit. 176,038, March 30, 1922; *Cent.* **1923**, II 1252. (6) Helberger, von Rebay, *Ann.* **531**, 283–284 (1937). (7) Helberger, *Ann.* **529**, 216–217 (1937). (8) Lock, Böck, *Ber.* **70**, 920 (1937). (9) Jensen, Rethwisch, *J. Am. Chem. Soc.* **50**, 1145, 1149 (1928). (10) Sharp, Sutherland, Wilson, *J. Chem Soc* **1943**, 346.

3:6625 *o*-CHLOROBENZAL (DI)CHLORIDE $C_7H_5Cl_3$ Beil. V - 300
(*o*-Chlorobenzylidene (di)chloride) V_1—
V_2—



B.P. 228.5°	(1)	$D_{15}^{15} = 1.399$ (1)	$n_D^{16} = 1.5670$ (4)
227–230°	(2)		
226–228° at 745 mm.	(3)		
100° at 10 mm.	(3)		

[For prepn of C̄ from *o*-chlorobenzaldehyde (3:6410) with PCl_5 (86% yield (3)) (5) see indic. refs.; from *o*-toluenesulfonyl chloride with Cl_2 at 92° (73.5% yield (4)) or at 150–200° (6) see indic. refs.; from *o*-chlorotoluene (3:8245) with Cl_2 (1) in pres. of PCl_5 at 150–180° (7) or in pres. of PCl_3 at 102–105° (8) see indic. refs.; from *o*-hydroxybenzaldehyde (salicylaldehyde) (1:0205) with PCl_5 see (2); for formn. of C̄ (5–7%) from benzal dichloride (3:6327) with Cl_2 in pres. of I_2 (accompanied by 43% *m*- and 46–47% *p*-isomers) see (9).]

[For use of C̄ in prepn. of triphenylmethane dyes see (10) (11); for condensation with isoviolanthrone in prepn. of vat dyes see (12).]

C̄ on boilg. with water for 20 hrs. (3) or on htg. with aq in s.t. at 170° (2) or with weakly fumg H_2SO_4 at ord. temp. as directed (7) yields *o*-chlorobenzaldehyde (3:6410). [For studies of this hydrolysis under various other conditions see (13) (5).]

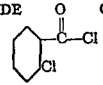
C̄ on oxidn. with CrO_3 (2), or C̄ on boilg. with aq. for 20 hrs. followed by treatment with cold conc. aq. $KMnO_4$ (3), gives (75% yield (3)) *o*-chlorobenzoic acid (3:4150), m.p. 141° (3).

[C̄ in MeOH treated with molecular Ag + sand and htd. in s.t. for 6 hrs. at 95° yields (1) α,β-dichloro-α,β-*bis*-(*o*-chlorophenyl)ethane [Beil. V-601], cryst. from ether + lgr., m.p. 170.5° (1).]

3:6625 (1) Gill, *Ber.* **26**, 650–652 (1893). (2) Henry, *Ber.* **2**, 136 (1869). (3) Asinger, Lock, *Monatsh* **62**, 333–334 (1933). (4) Davies, Dick, *J. Chem. Soc.* **1932**, 2045. (5) Olivier, Weber, *Rec. trav. chim.* **53**, 881, 888 (1934). (6) Gilliard, Monnet, Cartier, Ger. 98,433, Dec. 12, 1896, *Cent.* **1898**, II 800. (7) Erdmann, *Ann.* **272**, 151–152 (1892). (8) Kyrides (to National Aniline and Chem. Co), U S 1,733,268, Oct. 29, 1929; *Cent.* **1930**, I 3831. (9) Wertyporoch, *Ann.* **493**, 161–162 (1932) (10) Geigy and Co., Ger. 213,503, Oct. 14, 1909; *Cent.* **1909**, II 1515.

(11) Weiler, Wenk, Stötter, Ger. 540,208, Dec. 12, 1931; *Cent.* **1932**, I 3013. (12) Wuertz, Lycan (to du Pont Co), U.S. 2,082,560, June 1, 1937; *Cent.* **1937**, II 2077; *C.A.* **31**, 5595 (1937). (13) Lock, Asinger, *Monatsh.* **59**, 157–160 (1932).

3:6640 *o*-CHLOROBENZOYL CHLORIDE $C_7H_4OCl_2$ Beil. IX - 336 IX$_1$-(139)



B.P.		B.P. (*cont.*)			
229–230° at 773 mm.	(1)	114.5°	at 19.75 mm.	(15)	F.P. −4° (1)
235–238°	(2)	110°	at 15 mm.	(8)	
228–236° at 760 mm.	(3)	108°	at 14.5 mm.	(15)	
233°	(4)	105°	at 12.75 mm.	(15)	
227°	(11)	104.8–105.2°	at 12.5 mm.	(9)	
224–224.5°	(5)	103.5°	at 12 mm.	(15)	
224°	(6)	101.5°	at 11 mm.	(15)	
137–139° at 60 mm.	(7)	93–95°	at 10 mm.	(7)	
122° at 26.5 mm.	(15)	87°	at 9 mm.	(10)	
		78.9–79.2°	at 2 mm.	(36)	

[For prepn. of C̄ from *o*-chlorobenzoic acid (3:4150) with PCl_5 (78% yield (11)) (2), with $PCl_3 + ZnCl_2$ (78% yield (11)), with $SOCl_2$ (yield: 90–98% (11), 87% (10)) (12) (13) (36), or with *o*-chlorobenzotrichloride (3:6880) + $ZnCl_2$ (14) see indic. refs.; from *o*-chlorobenzaldehyde (3:6410) with Cl_2 at 140–160° (70–72% yield) see (7); from toluene-*o*-sulfonyl chloride with $SOCl_2$ in s.t. at 240° (41% yield) see (4).]

[For formn. of C̄ (together with other products) from benzoyl chloride (3:6240) with $Cl_2 + FeCl_3$ (14.5% C̄) (15) (16), from *o*-hydroxybenzoic acid (salicylic acid) (1:0780) with PCl_5 (17) (18) or with phosgene (3:5000) + pyridine in toluene at 60–80° (19); from sodium salicylate with PCl_5 (18) (20); from *o*-sulfobenzoic acid dichloride by distn. at ord. press. (21) (8) (22) (3) see indic. refs.]

[C̄ with MeOH yields (1) methyl *o*-chlorobenzoate (3:6695) (for study of rate of reaction see (6)); C̄ with EtOH yields (23) ethyl *o*-chlorobenzoate (3:6800) (for study of rate of reaction see (5)).]

[C̄ with Na *o*-chlorobenzoate should yield *o*-chlorobenzoic acid anhydride, ndls. from lt. pet. (25) or alc. (26), m.p. 79.6° (25), 78–79° (26); this anhydride also results from *o*-chlorobenzoic acid with P_2O_5 in boilg. toluene (25) or with oxalyl dichloride (3:5060) in boilg. C_6H_6 (26).]

[C̄ on cat. hydrogenation gives (70% yield (27)) (28) *o*-chlorobenzaldehyde (3:6410).]

[For reactn. of C̄ with $AlCl_3$ + benzene yielding (29) *o*-chlorobenzophenone (3:0715), with $AlCl_3$ + *o*-chlorotoluene yielding (30) 2,3-dichloro-4-methylbenzophenone, with $AlCl_3$ + *p*-dichlorobenzene yielding (31) 2,2′,5′-trichlorobenzophenone, with $AlCl_3$ + naphthalene yielding (32) α-naphthyl *o*-chlorophenyl ketone, or with anisole + $AlCl_3$ (1:7445) yielding (33) 2-chloro-4-methoxybenzophenone see indic. refs.]

[For reactn. of C̄ with perylenetetracarboxylic acid diimide (34) or with aminodibenzanthrones (35) yielding vat dyes see indic. refs.]

C̄ on hydrolysis yields *o*-chlorobenzoic acid (3:4150), m.p. 141°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *o*-chlorobenzoic acid (3:4150).

3:6640 (1) Montagne, *Rec. trav. chim.* **19**, 55–56 (1900). (2) Emmerling, *Ber.* **8**, 883 (1875). (3) Davies, Dick, *J. Chem. Soc.* **1932**, 2044. (4) Pollak, Rudich, *Monatsh.* **43**, 217–218 (1922). (5) Norris, Fasce, Staud, *J. Am. Chem. Soc.* **57**, 1415–1420 (1935). (6) Norris, Young, *J. Am. Chem. Soc.* **57**, 1420–1424 (1935). (7) Clarke, Taylor, *Org. Syntheses*, Coll. Vol. **1** (2nd ed.), 155–156 (1941); (1st ed.), 148–149 (1932); **9**, 34–35 (1929). (8) Fritsch, *Ber.* **29**, 2299 (1896). (9) Kohlrausch, Pongratz, Stockmair, *Monatsh.* **67**, 108 (1935). (10) Novello, Miriam, Sherwin, *J. Biol. Chem.* **67**, 557 (1926).

(11) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (12) Frankland, Carter, Adams, *J. Chem. Soc.* **101**, 2476 (1912). (13) Meyer, *Monatsh.* **22**, 427 (1901). (14) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929, *Cent* **1929**, II 1348; *C.A.* **24**, 129 (1930). (15) Hope, Riley, *J. Chem. Soc.* **121**, 2510–2527 (1922). (16) Hope, Riley, *J. Chem.* ... a, *Ann.* **83**, 317–318 (1852). (18) Kolbe, Lautermann, ... em. Ind Basel, Brit. 401,643, Dec. 14, 1933; *Cent.* **1934**, ... *Cent.* **1934**, I 287. (20) Reichenbach, Beilstein, *Ann.* **132**, 311–313 (1864).

(21) Remsen, Kohler, *Am. Chem. J.* **17**, 332–333 (1895). (22) List, Stein, *Ber.* **31**, 1653–1654 (1898) (23) Kekulé, *Ann* **117**, 153–154 (1861). (24) Berger, Olivier, *Rec. trav. chim.* **46**, 516–527 (1927). (25) Rule, Paterson, *J. Chem. Soc.* **125**, 2161 (1924). (26) Adams, Wirth, ...

—— **2,3,4-TRICHLOROTOLUENE**

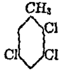
$C_7H_5Cl_3$

Beil. V - 298
V_1—
V_2-(232)

B.P. 231–232° at 716 mm. **M.P. 41°**

See **3:0425.** *Division A. Solids.*

—— **2,3,5-TRICHLOROTOLUENE**



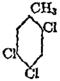
$C_7H_5Cl_3$

Beil. V - 299
V_1—
V_2—

B.P. 229–231° at 757 mm. **M.P. 45–46°**

See 3:0610. *Division A· Solids.*

—— **2,4,5-TRICHLOROTOLUENE**



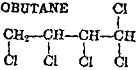
$C_7H_5Cl_3$

Beil. V - 299
V_1-(152)
V_2-(232)

B.P. 229–230° at 716 mm. **M.P. 82°**

See **3:2100.** *Division A: Solids.*

—— **1,1,2,3,4-PENTACHLOROBUTANE**
(Solid diastereoisomer)



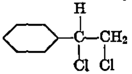
$C_4H_5Cl_5$

Beil. S.N. 10

B.P. 230° **M.P. 49°** **D_-^{53} = 1.539** **n_D^{53} = 1.5065**

See **3:0750.** *Division A: Solids.*

3:6685 *d,l*-1,2-DICHLORO-1-PHENYLETHANE $C_8H_8Cl_2$ Beil. V - 354
(α,β-Dichloroethylbenzene; styrene dichloride) V_1—
V_2-(278)



B.P.				
233–234°	at 759 mm. (1)	$D_4^{15} = 1.240$ (1)		$n_D^{15} = 1.5544$ (1)
114.5–115.5°	at 15 mm. (1)			
93°	at 5 mm. (2)			

Limpid liq. with faint odor.

[For prepn. of C̄ from phenylethylene (styrene) (1:7435) with Cl_2 in $CHCl_3$ at 0° (1) cf. (3) or in CCl_4 at 40–50° (4) (note that some β-chlorostyrene (3:8717) is also formed (4)) see indic. refs.; for formn. of C̄ in reaction of styrene (1:7435) with NCl_3 in CCl_4 at −10° (5) or from ethylbenzene (1:7410) with Cl_2 in bright sunlight (6) see indic. refs.]

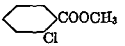
[C̄ with a mildly alkaline agent such as Na_2CO_3, NaOAc, CaO, or $CaCO_3$ (but not alkali hydroxide) as directed (7) undergoes hydrolysis of its α-chlorine atom giving chloromethylphenyl-carbinol (styrene chlorohydrin) (3:9570).]

[C̄ passed over activated Al_2O_3 at 360–400° and 85–105 mm. pres. (4) or C̄ with pyridine as directed (8) loses HCl giving (92% yield (4)) β-chlorostyrene (3:8717).]

[C̄ with aq. alc. NaOH at 50–60° for 4 hrs. loses HCl (in the opposite sense from preceding paragraph) giving (89% yield (4)) α-chlorostyrene (3:8715).]

3:6685 (1) Biltz, *Ann.* **296**, 275–277 (1897). (2) Knorr (to I.G.), Ger. 559,521, Sept. 21, 1932; *Cent.* **1933**, I 1843; *C.A.* **27**, 736 (1933): French 735,000, Oct. 31, 1932; *Cent.* **1933**, I 1843, *C.A.* **27**, 1011 (1933). (3) Blyth, Hofmann, *Ann.* **53**, 309–310 (1845). (4) Emerson, Agnew, *J. Am. Chem. Soc.* **67**, 518–520 (1945). (5) Coleman, Campbell, *J. Am. Chem. Soc.* **50**, 2754–2755 (1928). (6) Evans, Mabbott, Turner, *J. Chem. Soc.* **1927**, 1163. (7) I.G., French 735,108, Nov. 3, 1932; *Cent.* **1933**, II 1093; *C.A.* **27**, 1011 (1933). (8) I.G., French, 729,730, July 30, 1932; *Cent.* **1932**, II 3015; *C.A.* **27**, 307 (1933).

3:6695 METHYL *o*-CHLOROBENZOATE $C_8H_7O_2Cl$ Beil. IX - 336
IX_1—



B.P.			
234–235°	at 762.4 mm. (1)		
233–236°	at 760 mm. (8)		
229–230°	(2)		$n_D^{22} = 1.535$ (8)
119.5–120.5	at 24.4 mm. (3)		
119°	at 19 mm. (4)		
111–113°	at 14 mm. (8)		
113–115°	at 11 mm. (5)		

[For prepn. of C̄ from *o*-chlorobenzoic acid (3:4150) with MeOH + HCl (2) or MeOH + H_2SO_4 (2) (5) or MeOH + $BF_3.Et_2O$ (70.6% yield (4)) see indic. refs.; from *o*-chlorobenzoyl chloride (3:6640) with MeOH see (1).]

C̄ on htg. with sirupy H_3PO_4 at 200° yields (6) *o*-chlorobenzoic acid (3:4150), chlorobenzene (3:7903), dimethyl ether + CO_2.

C̄ added to 5–6 pts. very conc. HNO_3 at 0°, poured onto ice, yields (1) mainly methyl 2-chloro-5-nitrobenzoate [Beil. IX-403], ndls. from MeOH, m.p. 73° (1).

[C̄ with Na + methyl acetate condenses giving (65–70% yield (5)) methyl *o*-chlorobenzoylacetate, b.p. 170–172° at 12 mm. (5); this prod. with excess phenylhydrazine in

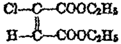
alc. + AcOH gives on htg. 3-(*o*-chlorophenyl)-1-phenylpyrazolone-5, colorless ndls. from MeOH, m.p. 113–114° (5); corresp. prod. from *p*-nitrophenylhydrazine, m.p. 203–204° (5).]

C̄ on hydrolysis (Sap. Eq. = 170.5) yields methyl alcohol (1:6120) + *o*-chlorobenzoic acid (3:4150). [*For studies of hydrolysis under various cond. see* (2) (3) (7).] — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *o*-chlorobenzoic acid (3:4150).

... las, *Z. physik. Chem.* **24**, ... (4) Sowa, Nieuwland, ... **10**, 9–13, 17–18 (1928). ... ombie, Scarborough, *J. Chem. Soc.* **123**, 2695–2697 (1923); **125**, 2593–2594 (1924). (8) Kahovec, Wagner, *Monatsh.* **74**, 284 (1943).

3:6697 DIETHYL CHLOROMALEATE

$C_8H_{11}O_4Cl$ Beil. II - 753, II_1-(305), II_2-(646)



B.P.				
235°	at 760 mm., sl. dec. (1)	$D_{4\ vac.}^{25} = 1.1914$ (2)		
189.5–190.5°	at 210 mm. (1)			
125.5° cor.	at 19 mm. (2)	$D_4^{20} = 1.174$	(4) (5)	$n_{He}^{20} = 1.455$ (4)
122°	at 15 mm. (3)			1.4549 (5)
120°	at 12 mm. (5)			
		$D_4^{19} = 1.1754$	(4)	$n_{He}^{19} = 1.45532$ (4)

[*See also diethyl chlorofumarate* (3:6864).]

Colorless oil with pleasant odor.

[For prepn. of C̄ from chloromaleic anhydride (3:0280) in abs. EtOH with conc. H_2SO_4 in cold (4) or on refluxing several hrs. (6) or from silver salt of chloromaleic acid (3:3432) with EtI (1) (3) *see indic. refs.*]

[C̄ (1 mole) with ethyl sodioacetoacetate (1 mole) in abs. alc. refluxed ½ hr. reacts readily yielding (3) (7) triethyl γ-*acetylaconitate* [Beil. III-860], *yel. oil*, b.p. 187–188° at 15 mm. (3), the same prod. as similarly obtd. from diethyl chlorofumarate (3:6864).]

[C̄ with 6% alc. NH_3 (2 moles) at ord. temp. for 5–6 days reacts to yield (6) diethyl iminosuccinate (diethyl aminobuten-2-dioate) [Beil. III-784], b.p. 144–145° at 25 mm. (6), identical with the prod. from similar treatment of the isomeric diethyl chlorofumarate (3:6864) q v.]

3:6697 (1) Perkin, *J. Chem. Soc.* **53**, 708 (1888). (2) Walden, Swinne, *Z. physik. Chem.* **79**, 742 ... (1896). (4) von Auwers, Harres, *Ber.* ... *physik. Chem.* **A-143**, 10 (1929). (6) ... (7) Ruhemann, *J. Chem. Soc.* **71**, 323–324 (1897).

3:6700 *p*-CHLOROBENZAL (DI)CHLORIDE

(*p*-Chlorobenzylidene dichloride)

$C_7H_5Cl_3$ Beil. V - 300, V_1—, V_2-(232)

B.P.		
236°	at 755 mm.	(1)
234°		(2)
127–132°	at 22 mm.	(3)
108°	at 10 mm.	(1)

[For prepn. of C̄ from p-chlorobenzaldehyde (3:0765) with PCl_5 see (1) (4); from p-toluenesulfonyl chloride with $SOCl_2$ in s.t. at 140° for 18 hrs. (54% yield (3)) or with Cl_2 at 150–200° (accompanied by p-chlorobenzotrichloride (3:6825) (5)) see indic. refs.; for formn. of C̄ (47% (6)) from benzal dichloride (3:6327) with Cl_2 in pres. of I_2 (6) (2) (accompanied by 5–7% o- and 43% m-isomers (6)) see indic. refs.]

[For use of C̄ in prepn. of triphenylmethane dyes see (7).]

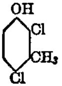
C̄ on refluxing with aq. for 20 hrs. (1) or on htg. with aq. in s.t. at 170° (2) yields p-chlorobenzaldehyde (3:0765). [For studies of this hydrolysis under various other conditions see (4) (1).]

C̄ on oxidn. with CrO_3 (2), or C̄ on refluxing with aq. for 20 hrs. followed by treatment with cold conc. aq. $KMnO_4$ (1), gives (85% yield (1)) p-chlorobenzoic acid (3:4940), m.p. 240° (1).

[For behavior of C̄ with MeMgCl see (8).]

3:6700 (1) Asinger, Lock, *Monatsh.* **62**, 336 (1933). (2) Beilstein, Kuhlberg, *Ann.* **146**, 327–329 (1868). (3) Pollak, F [illegible]
53, 881, 888 (1934).
(6) Wertyporoch, *An* [illegible]
1931; *Cent.* **1932**, I 30

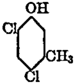
—— **2,4-DICHLORO-3-METHYLPHENOL** $C_7H_6OCl_2$ Beil. VI — VI_1— VI_2-(356)



B.P. 235–236° at 745 mm. M.P. 58–59°

See 3:1205. *Division A: Solids.*

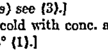
—— **4,6-DICHLORO-3-METHYLPHENOL** $C_7H_6OCl_2$ Beil. VI — VI_1— VI_2-(356)



B.P. 235–236° M.P. 71–72°

See 3:1745. *Division A: Solids.*

3:6710 m-**CHLOROBENZAL (DI)CHLORIDE** $C_7H_5Cl_3$ **Beil. S.N. 466**
(m-Chlorobenzylidene dichloride)



B.P. 235–237° at 738 mm. (1)
105° at 11 mm. (1)

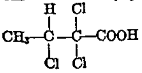
Colorless liq. with agreeable odor.

[For prepn. of C̄ from m-chlorobenzaldehyde (3:6475) with PCl_5 (75% yield (1)) (2) see indic. refs.; for formn. of C̄ from benzal dichloride (3:6327) with Cl_2 in pres. of I_2 (43% C̄ together with 5–7% o- and 46% p-isomers) see (3).]

C̄ on refluxing 20 hrs. with aq. then treated in cold with conc. aq. $KMnO_4$ gives (70% yield (1)) m-chlorobenzoic acid (3:4392), m.p. 158° (1).]

3:6710 (1) Asinger, Lock, *Monatsh.* **62**, 334–336 (1933). (2) Olivier, Weber, *Rec. trav. chim.* **53**, 882, 888 (1934). (3) Wertyporoch, *Ann.* **493**, 161–162 (1932).

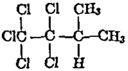
—— α,α,β-TRICHLORO-*n*-BUTYRIC ACID $C_4H_5O_2Cl_3$ Beil. II - 280
II_1-(124)
II_2-(255)



B.P. 236–238° M.P. 60°

See 3:1280. *Division A: Solids.*

3:6725 3,3,4,4,4-PENTACHLORO-2-METHYLBUTANE $C_5H_7Cl_5$ Beil. I - 136
I_1—
I_2—

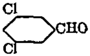


B.P. 235–240° (1)

[For prepn. of C̄ from diisoamyl sulfide [Beil. I-405, I_1-(200), I_2-(435)] by actn. of Cl_2 see (1).]
C̄ on htg. 7 hrs. at 110° in a s.t. with Ag_2O and aq. yields (1) CO_2 + isobutyric acid (1:1030) (as AgĀ).

3:6725 (1) Spring, Lecrenier, *Bull. soc. chim.* (2) 48, 627–628 (1887).

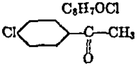
—— 3,5-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. S.N. 635



B.P. 235–240° at 748 mm. M.P. 65°

See 3:1475. *Division A: Solids.*

3:6735 *p*-CHLOROACETOPHENONE C_8H_7OCl Beil. VII - 281
(p-Chlorophenyl methyl ketone) VII_1-(151)



B.P.			M.P.		
236.5°	cor. at 740 mm.	(1)	20.5°	(10) (11) (12)	D_4^{20} = 1.188 (2)
232°		(2) (3)	20–21°	(5) (1)	
231–232°		(4) (17)	20°	(2)	
124–126°	at 24 mm.	(5)	19.8°	(13)	
113°	at 14 mm.	(3)	19°	(14)	
108–111°	at 13 mm.	(6)	17.6–17.8°	(15)	
152°	at 12 mm.	(7)			
99°	at 7 mm.	(1)			
89.4–91°	at 5 mm.	(8)			

Insol. aq.; misc. alc. or ether. — C̄ does *not* yield an addn. prod. with $NaHSO_3$.
[For prepn. of C̄ from chlorobenzene (3:7903) with Ac_2O + $AlCl_3$ in CS_2 (yields: 83–79% (15), 78–74% (5), 68–66% (1)) (8) (9) or with acetyl chloride (3:7065) + $AlCl_3$ in absence

of solvent (poor yield (2)) or in CS_2 (yields: 80–90% (16), 81% (6), 41% (17)) see indic. refs.; from p-chlorobenzoylacetic acid on warming (18); from methyl p-chlorobenzoylacetate (4) on ketonic hydrolytic cleavage by boilg. 10–12 hrs. with 20% H_2SO_4 see (4).]

[$\bar{C}$ in CS_2 treated with 1 mole Cl_2 yields (19) p-chlorophenacyl chloride (3:2990), m.p. 101°; $\bar{C}$ with 2 moles Cl_2 at 50–60° without solv. (19) yields 4,ω,ω-trichloroacetophenone [Beil. VII-283], m.p. 57°. — $\bar{C}$ with 1 mole Br_2 in CS_2 or AcOH yields (17) (20) p-chlorophenacyl bromide [Beil. VII-285], cryst. from alc., m.p. 96.5° (20), 96° (17) (for studies of rate of bromination see (13), of influence of light and other factors see (21)); $\bar{C}$ with excess Br_2 directly (22), in AcOH (17), or in CCl_4 susp. of $CaCO_3$ (22) yields 4-chloro-ω,ω-dibromoacetophenone [Beil. VII-286], m.p. 93.5–94.5° (22), 92.5° (17).] [Note proximity of this m.p. to that (96°) of p-chlorophenacyl bromide (above).]

[$\bar{C}$ on mononitration with mixt. of conc. HNO_3 + conc. H_2SO_4 at −10° as directed (6) or added slowly to 10 pts. HNO_3 ($D = 1.5$) at 0° (23) yields 4-chloro-3-nitroacetophenone, *ndls. from alc., m.p. 104° (6), 99–101° (23) (accompanied in the former case (6)* by a little 4-chloro-3-nitrobenzoic acid, m.p. 181°).]

$\bar{C}$ in alk. medium readily condenses with aldehydes: e.g., $\bar{C}$ in dil. alc. with a little alk. gives (yields: 96% (24), 93% (25), 83% (7)) benzal p-chloroacetophenone (p-chlorochalcone), cryst. from ether of $CHCl_3$, m.p. 101° (24), 98.5° (7), 96.4° (12), 96° (25) (for study of rate of condensation see (12)); similarly $\bar{C}$ with salicylaldehyde (1:0205) yields (23) salicylidene-p-chloroacetophenone, yel. ndls. from alc., m.p. 151° (23); $\bar{C}$ with p-dimethylaminobenzaldehyde yields (26) p-dimethylaminobenzal-p-chloroacetophenone, yel. ndls. from alc., m.p. 140–140.5° (26); for corresp. condensation of $\bar{C}$ with p-chlorobenzaldehyde (3:0765) see (16), with o-nitrobenzaldehyde see (27) (28).

[$\bar{C}$ also readily condenses with esters: e.g., $\bar{C}$ in abs. alc. + NaOEt treated with ethyl formate (1:3000) gives (28) hydroxymethylene-p-chloroacetophenone, yel. ndls. from pet. eth., m.p. 48–49° (28); $\bar{C}$ with ethyl phenylacetate (1:3872) in ether with Na gives (40% yield (29)) ω-(phenylacetyl)-p-chloroacetophenone.]

[$\bar{C}$ with PCl_5 at 100° for 4 hrs. gives (60% yield (30)) p,α-dichlorostyrene, b.p. 115–116° at 20 mm., m.p. −6 to −5°, $D_{-}^{25} = 1.247$, $n_D^{25} = 1.5735$ (30); $\bar{C}$ with selenium oxychloride ($SeOCl_2$) gives (50% yield (31)) *bis*-(p-chlorophenacyl)selenium dichloride, m.p. 126° (31); $\bar{C}$ with K pyrosulfate + a little conc. H_2SO_4 htd. at 80° for 4 hrs. (46% yield (32)) or $\bar{C}$ with 1% I_2 htd. 4 hrs. at 170° (32) gives 1,3,5-*tris*-(p-chlorophenyl)benzene, white ndls. from AcOEt, m.p. 238° (32); for behavior of $\bar{C}$ with NOCl see (33) (14), with NaOEt + amyl nitrite in alc. see (34) (35).]

[$\bar{C}$ htd. as directed with excess NH_4 formate and the intermediate formyl deriv. hydrolyzed with HCl gives (yields: 82% (36), 65% (37)) *d,l*-α-(p-chlorophenyl)ethylamine, b.p. 105° at 10 mm., $D_{20}^{20} = 1.1178$, $n_D^{25} = 1.5420$ (hydrochloride, m.p. 192–193°, *N*-benzoyl deriv., m.p. 144–145° (36)).]

[$\bar{C}$ on htg. with 10% aq. NaOH + Cu at 190° for 5 hrs. under press. yields (38) p-hydroxyacetophenone (1:1527), m.p. 109°; $\bar{C}$ with conc. aq. NH_4OH in pres. of Cu_2O htd. 5 hrs. at 220° under press. yields (39) p-aminoacetophenone [Beil. XIV-46, XIV_1-(366)]; $\bar{C}$ on htg. with 50% KOH as directed (40) gives small yield of p-chlorobenzoic acid (3:4940); $\bar{C}$ with alc. NaOEt htd. in s.t. at 130°–140° gives (41) p-chlorophenyl-methyl-carbinol, p-chlorobenzoic acid, and other prods.]

$\bar{C}$ on oxidn. with $KMnO_4$ (2) or in MeOH soln. with NaOH + Cl_2 (93% yield (42)) or with CrO_3 + H_2SO_4 (95% yield (43)) or by cat. vapor-phase oxidn. (90% yield (44)) gives p-chlorobenzoic acid (3:4940), m.p. 242°. [Note that $\bar{C}$ in abs. alc. refluxed with SeO_2 gives (45) p-chlorophenylglyoxal, m.p. 122° (for study of rate see (46)).]

Ⓓ *p*-Chloroacetophenone oxime: ndls. from alc., m.p. 95° (17). [This prod. with conc.

H_2SO_4 htd. at 100° rearranges to acet-*p*-chloroanilide [Beil. XII-611, XII_1-(306)], m.p. 172–173° (17).]

Ⓓ *p*-Chloroacetophenone phenylhydrazone: m.p. 114° (17), 112–113° (48) (decomposes on stdg. 2 days (17) (4).)

Ⓓ *p*-Chloroacetophenone *p*-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 239° (4).

Ⓓ *p*-Chloroacetophenone 2,4-dinitrophenylhydrazone: scarlet cryst., m.p. 231° cor. (47).

Ⓓ *p*-Chloroacetophenone semicarbazone: white cryst. from 40% AcOH, m.p. 200–201° (4).

3:6735 (1) Noller, Adams, *J. Am. Chem Soc.* **46**, 1893 (1924). (2) Gautier, *Ann. chim.* (6) **14**, 372–375 (1888). (3) Kahovec, Wagner, *Proc. Indian Acad Sci.* **A-8**, 325 (1938). (4) Wahl, Rolland, *Ann. chim.* (10) **10**, 27–31, 34–35 (1928) (5) Adams, Noller, *Org. Syntheses*, Coll. Vol. 1 (2nd ed.), 111 (1941), (1st ed.), 105 (1932), **5**, 19 (1925) (6) Mayer, Stark, Schön, *Ber.* **65**, 1334 (1932). (7) Bergmann, Hampson, *J. Chem. Soc.* **1935**, 991. (8) Groggins, U.S., 1,991,743, Feb. 19, 1935; *Cent.* **1936**, I 853, *C.A.* **29**, 2175 (1935). (9) Groggins, U.S. 2,008,418, July 16, 1935; *Cent.* **1936**, I 1500; *C.A.* **29**, 5856 (1935). (10) Hassel, Naeshagen, *Z. physik. Chem.* **B-15**, 419 (1932).

(11) Evans, Morgan, Watson, *J. Chem. Soc.* **1935**, 1172. (12) Coombs, Evans, *J. Chem Soc.* **1940**, 1295 (13) Nathan, Watson, *J. Chem Soc.* **1933**, 220. (14) Edkins, Linnell, *Quart. J.* ... ggins, ... (17) ... , 1262 (1915). (19) Ref. 2, pp. 395–396, 402. (20) Judefind, Reid, *J. Am. Chem. Soc.* **42**, 1044–1045 (1920).

(21) Sampey, Hicks, *J. Am. Chem Soc* **63**, 1098–1101 (1941) (22) Fisher, *J. Am. Chem. Soc.* **55**, 4595 (1933). (23) C. G. LeFèvre, R. J. W. LeFèvre, *J. Chem. Soc.* **1932**, 1989–1992. (24) Dilthey, *J. prakt. Chem.* (2) **101**, 199 (1920). (25) Allen, Frame, *Can. J. Research* **6**, 605–613 (1932), *Cent.* **1932**, II 3880; *C.A.* **26**, 5086 (1932). (26) Pfeiffer, Kleu, *Ber.* **66**, 1706 (1933). (27) Tanasescu, Baciu, *Bull. soc. chim.* (5) **4**, 1748–1749; 1677–1678 (1937) (28) Benary, *Ber.* **61**, 2253 (1928). (29) Kohler, Smith, *J. Am. Chem. Soc.* **44**, 630 (1922). (30) Vaughn, Nieuwland, *J Am. Chem Soc* **56**, 1208 (1934).

(31) Nelson, Jones, *J. Am. Chem. Soc.* **52**, 1589 (1930). (32) Bernhauer, *J. prakt. Chem.* (2) **145**, 305 (1936). (33) Rheinboldt, Schmitz-Dumont, *Ann.* **444**, 129 (1925). (34) Avogadro, ... (36) Ingersoll, Brown, Ingersoll, *Org. Syntheses*, ... em. Co.), U.S 1,961,630, ... Bryner (to Dow Chem. ... 934). (40) Lock, Böck, *Ber.* **70**, 921 (1937).

(41) Gastaldi, Cherchi, *Gazz. chim. ital* **45**, II 271–273 (1915). (42) von Arendonk, Cupery, ... d. *Eng. Chem.* **27**, 1397 ... (45) Karrer, Musante, ... *Gen. Chem. (U.S.S.R.)* ... *Org. Chem.* **2**, 224 (1938).

3:6750 ETHYL *p*-CHLOROBENZOATE $C_9H_9O_2Cl$ Beil. IX - 340 IX_1-(140)

$D_4^{14.0} = 1.1873$ (8) $n_D^{14} = 1.52700$ (8)

B.P.		
238°		(1)
237.4–238.0°		(2)
142°	at 50 mm.	(3)
121–122°	at 16 mm.	(4)
122°	at 15 mm.	(5)
120.1–120.2°	at 15 mm.	(2)
118°	at 15 mm.	(6)
118°	at 14 mm.	(7)

[For prepn. of C̄ from p-chlorobenzoic acid (3:4940) with EtOH + H_2SO_4 see (1) (3); from p-chlorobenzoyl chloride (3:6550) with abs. EtOH see (2).]

C̄ in alc. soln. on htg. with hydrazine hydrate yields (9) (10) p-chlorobenzhydrazide, white ndls. from alc., m.p. 162–163° (10). [This prod. with BzH yields benzal p-chlorobenzhydrazide, ndls. from 95% alc., m.p. 227–229° (10).] [For use of p-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (10).]

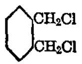
[C̄ (1.5 moles) with NaOEt (0.3 mole) at 160–180° for 1 hr. gives (75% yield (15)) di-(p-chlorobenzoyl)methane, cryst. from MeOH, m.p. 158–159° (15).]

C̄ on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + p-chlorobenzoic acid (3:4940). [For studies of hydrolysis of C̄ under various conditions see (7) (6) (11) (4) (12) (5) (13) (14).] For the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see p-chlorobenzoic acid (3:4940).

3:6750 (1) van Raalte, *Rec. trav. chim.* **18**, 398 (1899). (2) Kohlrausch, Stockmair, *Monatsh.* **66**, 325 (1935). (3) Bergmann, Engel, *Z. physik. Chem.* **B-15**, 95 (1932). (4) Kindler, *Ann.* **450**, 16 (1926). (5) Timm, Hinshelwood, *J. Chem. Soc.* **1938**, 866–869. (6) Cashmore, McCombie, Scarborough, *J. Chem. Soc.* **121**, 243–253 (1922). (7) McCombie, Scarborough, *J. Chem. Soc.* **107**, 159 (1915). (8) von Auwers, *Ann.* **422**, 166 (1921). (9) Kahl, *Cent.* **1904**, II 1493. (10) Shih, Sah, *Science Repts. Natl. Tsing-Hua Univ.* **A-2**, 353–357 (1934); *Cent.* **1935**, I 56–57; *C.A.* **29**, 466 (1935).

(11) McCombie, Scarborough, Settle, *J. Chem. Soc.* **121**, 2308–2318 (1922). (12) Blakey, McCombie, Scarborough, *J. Chem. Soc.* **1926**, 2867. (13) Westheimer, *J. Am. Chem. Soc.* **62**, 1893 (1940). (14) Price, Westheimer, *J. Chem. Phys.* **11**, 150–153 (1943). (15) McElvain, Weber, *J. Am. Chem. Soc.* **63**, 2196 (1941).

—— o-XYLYLENE (DI)CHLORIDE



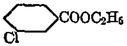
$C_8H_8Cl_2$

Beil. V - 364
V_1—
V_2-(283)

B.P. 239–241° **M.P. 55°**

See 3:1040. *Division A: Solids.*

3:6770 ETHYL m-CHLOROBENZOATE $C_9H_9O_2Cl$ Beil. IX - 337
IX_1-(139)



B.P.

[245°		(1)]
239.3–241.7°		(2)
130.0–130.5°	at 20–21 mm.	(3)
124°	at 21.5 mm.	(4)
121°	at 20 mm.	(5)
114.6–116.2°	at 15 mm.	(2)
119°	at 13 mm.	(6)

$D_4^{15.4} = 1.1859$ (7) $n_D^{15.4} = 1.52233$ (7)

[For prepn. of C̄ from m-chlorobenzoic acid (3:4392) with EtOH + H_2SO_4 (1) or with 5% EtOH/HCl (90% yield (8)) see indic. refs.; from m-chlorobenzoyl chloride (3:6590) with EtOH see (1) (2).]

[C̄ on electrolytic reductn. in alc./H_2SO_4 soln. yields (9) m-chlorobenzyl ethyl ether [Beil. VI-444], b.p. 219° (9).]

C̄ on refluxing with hydrazine hydrate gives (97% yield (8)) m-chlorobenzhydrazide, ndls. from aq. or alc., m.p. 158° (8), 157–158° (10). [This prod. in aq. soln. on htg. with BzH + a few drops AcOH yields benzal-m-chlorobenzhydrazide, flocks from alc., m.p. 118°

(8) (10).] [For study of prepn. and use of *m*-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (10).]

C̄ on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + *m*-chlorobenzoic acid (3:4392). [For studies of hydrol. of C̄ under various cond. see (6) (11) (5).] — For the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *m*-chlorobenzoic acid (3:4392).

3:6770 (1) Limpricht, von Uslar, *Ann.* **102**, 262 (1857). (2) Kohlrausch, Stockmair, *Monatsh.* **66**, 324 (1935). (3) Kindler, *Ann.* **450**, 17 (1926). (4) Curtius, Melsbach, *J. prakt. Chem.* (2) **81**, 536 (1910). (5) Evans, Gordon, Watson, *J. Chem. Soc.* **1937**, 1430–1432. (6) McCombie, [illegible] (7) von Auwers, *Ann.* **422**, 166 (1921). (8) Curtius, [illegible] (9) Mettler, *Ber.* **37**, 3693 (1904). (10) Sah, [illegible] 443–449 (1936); *Cent* **1936**, II 2130; *C.A.* **30**, 8148 (1936).
(11) Blakey, McCombie, Scarborough, *J. Chem. Soc.* **1926**, 2867.

3:6775 γ-CHLORO-β-HYDROXY-*n*-PROPYL ACETATE $C_5H_9O_3Cl$ Beil. II - 142
II_1-(67)
II_2—

(Glycerol α-chlorohydrin α′-acetate; γ-aceto-α-chlorohydrin; γ-chloropropylene glycol α-acetate)

CH_2Cl
|
H—C—OH
|
$CH_2O.CO.CH_3$

B.P. **240°** (1) (2) at 760 mm. (3)
120–121° at 14 mm. (4)

[*See also glycerol α-chlorohydrin β-acetate* (3:6517).]

[For prepn. of C̄ from epichlorohydrin (3:5358) with AcOH in s.t. at 180° for 24 hrs. (1) (2) or in pres of anhydr. $FeCl_3$ at room temp. (4) cf. (5); note, however, that the isomeric glycerol α-chlorohydrin β-acetate (3:6517) is also formed.]

Note that the homogeneity of all reported prepns. of C̄ is probably open to serious question.

3:6775 (1) Reboul, *Ann. Suppl.* **1**, 232 (1861). (2) Bigot, *Ann. chim.* (6) **22**, 491 (1891). (3) Gibson, *J. Soc. Chem. Ind.* **50**, 950 (1931). (4) Knoevenagel, *Ann.* **402**, 136–138 (1914). (5) Delaby, Dubois, *Bull. soc. chim.* (4) **47**, 573 (1930).

3:6780 β-HYDROXYETHYL CHLOROACETATE $C_4H_7O_3Cl$ Beil. S.N. 160
(Ethylene glycol mono-(chloroacetate))

CH_2 CO.O.CH_2.CH_2
| |
Cl OH

B.P.				
240° dec.	at 760 mm. (1)	D_4^{20} = **1.330** (2)	n_D^{25} = **1.4585** (1)	
86°	at 1.6 mm. (2)	**1.324** (2)		
85°	at 0.15 mm. (1)		n_D^{20} = **1.46090** (2)	
84°	at 0.95 mm. (2)		**1.46049** (2)	
83°	at 0.08 mm. (1)			

Colorless odorless liq. — Miscible with aq. [dif. from ethylene glycol *bis*-(chloroacetate) (3:0720)].

[For prepn. of C̄ from ethylene oxide (1:6105) with chloroacetic acid (3:1370) in dry ether at 0° for 4 days (1) or at 50° for 6 days (2) see indic. refs.; from mono-sodium deriv. of ethylene glycol (1:6465) (1) or from ethylene glycol directly with chloroacetyl chloride (3:5235) in dry ether (1) or dioxane (2) see indic. *refs.*]

C̄ on stdg. in ord. glass gradually disproportionates into ethylene glycol (1:6105) and

ethylene glycol *bis*-(chloroacetate) (3:0720) (1); this disproportionation may also occur during reactions of C̄ and thus lead to numerous by-prods. (see below).

[C̄ with diazomethane gives (19% yield (1)) β-methoxyethyl chloroacetate (3:9285) accompanied by methyl chloroacetate (3:5585) and ethylene glycol *bis*-(chloroacetate) (3:0720).]

C̄ on long stdg. with aq. is slowly hydrolyzed into ethylene glycol (1:6465) and chloroacetic acid (3:1370) (2).

3:6780 (1) Allen, Hibbert, *J. Am. Chem. Soc.* **56**, 1398–1399 (1934). (2) Meerwein, Sönke, *J. prakt. Chem.* (2) **137**, 316–319 (1933).

3:6790 DI-(β-CHLOROETHYL) CARBONATE

(β,β′-Dichloroethyl carbonate)

$C_5H_8O_3Cl_2$

$Cl.CH_2CH_2O \backslash$
$\quad\quad\quad\quad\quad\quad\quad > CO$
$Cl.CH_2CH_2O /$

Beil. III —
III_1—
III_2-(5)

B.P.		M.P.		
240–241°	**(1)**	**+8.5° (1)**	D_4^{20} **= 1.3506 (1)**	n_D^{20} **= 1.4610 (1)**
115° at 8 mm. (1)				

Colorless odorless liq. — Insol. in boil. aq. and not decomposed thereby. — Volatile with steam (1). — Requires solid CO_2 + ether for solidification.

[For prepn. from β-chloroethyl chloroformate (3:5780) + ethylene chlorohydrin (3:5552) (70% yield) see (1).]

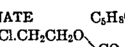
Hydrolyzes, but very slowly, even with warm alk. (1).

[For use as industrial solvent see (2) (3).]

3:6790 (1) Nekrassow, Komissarow, *J. prakt. Chem.* (2) **123**, 164 (1929). (2) I.G., French 785,705, Aug. 17, 1935; *Cent.* **1936**, I 1134. (3) I.G., Brit. 257,258, Aug. 11, 1926; *Cent.* **1927**, I 820.

3:6795 3,4-DICHLOROBENZYL CHLORIDE

$C_7H_5Cl_3$



Beil. V - 300
V_1—
V_2—

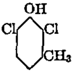
B.P. 241° (1)

[For prepn. of C̄ from 3,4-dichlorotoluene (3:6355) at b.p. or from benzyl chloride (3:8535) in pres. of I_2 on treatment with Cl_2 see (1).]

C̄ on oxidn. with CrO_3 yields (2) 3,4-dichlorobenzoic acid (3:4925) q.v.

3:6795 (1) Beilstein, Kuhlberg, *Ann.* **146**, 326–327 (1868). (2) Beilstein, Kuhlberg, *Ann.* **152**, 224–226 (1869).

—— 2,6-DICHLORO-3-METHYLPHENOL



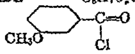
$C_7H_6OCl_2$

Beil. VI —
VI_1—
VI_2-(356)

B.P. 241° **M.P. 27°**

See 3:0150. *Division A: Solids.*

3:6797 3-METHOXYBENZOYL CHLORIDE $C_8H_7O_2Cl$ **Beil. X - 140**
(m-Anisoyl chloride) **X_1—**



B.P. 242.7–244.1°	at 760 mm.	(1)
242–243°	at 733 mm.	(2) (3)
148°	at 24 mm.	(4)
122–123°	at 16 mm.	(5)
123–125°	at 15 mm.	(6)
123°	at 11 mm.	(1)
110.8–111.0°	at 8.5 mm.	(7)
81.5–82.0°	at 1 mm.	(8)

[For prepn. of $\bar{C}$ from *m*-methoxybenzoic acid (1:0703) with PCl_5 (2) or with $SOCl_2$ (yields: 92% (6), 86% (4), 78% (5)) (1) (7) see indic. refs.]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous Na_2CO_3 + pyridine gives the corresp. anhydride, this reactn. is not specifically recorded for $\bar{C}$; however, 3-methoxybenzoic acid anhydride, cryst. from pet. eth., m.p. 66.6° (9), has been reported from 3-methoxybenzoic acid (1:0703) with P_2O_5 (9).]

[$\bar{C}$ with C_6H_6 + $AlCl_3$ (2) (said to be unsatisfactory because of autocondensation of $\bar{C}$ to anthracene derivs. (3)) or better with C_6H_5ZnBr (62% yield (6)) yields 3-methoxybenzophenone (1:5141), m.p. 37° (6) (2), b.p. 342–343° at 730 mm. (2), 192° at 14 mm. (6). — $\bar{C}$ with anisole (1:7445) + $AlCl_3$ in CS_2 (3) or in tetrachloroethane (5) gives (yields: 100% (5), 35% (3)) 3,4-dimethoxybenzophenone, pr. from alc., m.p. 58–59° (5), 55° (3).]

[$\bar{C}$ with ethyl sodioacetoacetate gives (61% yield (4) (10) ethyl *m*-methoxybenzoylacetoacetate; $\bar{C}$ with methyl sodio-α-ethylacetoacetate gives (10) methyl α-ethyl-α-(*m*-methoxybenzoyl)acetoacetate; $\bar{C}$ with ethyl sodio-α,γ-dimethoxyacetoacetate gives (11) ethyl α,γ-dimethoxy-α-(*m*-methoxybenzoyl)acetoacetate (for ketonic cleavage of these subst. acetoacetates see indic. refs.).]

[For reactn. of $\bar{C}$ with 1,4-diaminoanthraquinone in prepn. of vat dyes see (12) (13).]

[$\bar{C}$ with MeOH yields methyl *m*-methoxybenzoate (1:4111), b.p. 252°; $\bar{C}$ with EtOH yields ethyl *m*-methoxybenzoate (1:4131), b.p. 260° (for study of rate of reactn. of $\bar{C}$ with EtOH at 0° see (14) (8)).]

$\bar{C}$ on hydrolysis yields *m*-methoxybenzoic acid (1:0703), m.p. 109–110°.

3:6797 (1) Kahovec, Kohlrausch, *Z. physik. Chem.* **B-38**, 136 (1938). (2) Ullmann, Goldberg, *Ber.* **35**, 2813–2814 (1902). (3) Lea, Robinson, *J. Chem Soc.* **1926**, 2354–2355 (4) Robinson, Rose, *J. Chem. Soc.* **1933**, 1472. (5) Blicke, Weinkauff, *J. Am. Chem. Soc* **54**, 1449 (1932). (6) Martynoff, *Ann. chim.* (11) **7**, 437–438 (1937). (7) Thompson, Norris, *J. Am. Chem Soc.* **58**, 1956 (1936). (8) Norris, Young, *J. Am Chem. Soc.* **57**, 1424 (1936). (9) Rule, Patterson, *J. Chem. Soc.* **125**, 2161–2162. (10) Furukawa, *Sci Papers Inst Phys. Chem Research (Tokyo)* **24**, 320–324 (1934); *Cent.* **1935**, I 1071.

(11) Pratt, Robinson, *J. Chem. Soc.* **127**, 1185 (1925). (12) I.G., Swiss 136,249, Jan. 16, 1930, *Cent.* **1930**, II 3462. (13) B.A.S F., French 604,347, May 3, 1926; *Cent.* **1926**, II 2358. (14) Norris, Fasce, Staud, *J. Am. Chem. Soc.* **57**, 1415–1420 (1935).

—— ***p*-XYLYLENE DICHLORIDE**

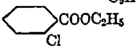
$C_8H_8Cl_2$ **Beil. V - 384**
V_1-(186)
V_2-(300)

B.P. 240–245° dec. **M.P. 100°**

See 3:2825. *Division A: Solids.*

3:6800 ETHYL o-CHLOROBENZOATE

$C_9H_9O_2Cl$ Beil. IX - 336
IX_1—



B.P. 242.8–244.0°		(1)	$D_4^{15.4} = 1.1942$ (9) $n_D^{15.4} = 1.52470$ (9)
243°		(2) (3)	
242°		(4)	
238–242°		(5)	
130°	at 20 mm.	(6)	
124.8–125.1°	at 20 mm.	(1)	
122.5°	at 15 mm.	(7) (8)	

[For prepn. of C̄ from o-chlorobenzoic acid (3:4150) with EtOH + HCl see (2); from o-chlorobenzoyl chloride (3:6640) with abs. EtOH see (5) (1).]

[C̄ on electrolytic reductn. in alc./H_2SO_4 soln. yields (10) mainly o-chlorobenzyl ethyl ether [Beil. VI-444; VI_1-(222)], b.p. 212° (10), together with a little o-chlorobenzyl alc. [Beil. VI-444; VI_1-(222)], ndls. from dil. alc., m.p. 72° (10).]

[C̄ with C_6H_5MgBr in ether as directed (11) yields α,α'-*bis*-(o-chlorophenyl)-α,α'-diphenylethylene glycol (*sym.*-2,2′-dichlorobenzpinacol) [Beil. VI_1-(523)].]

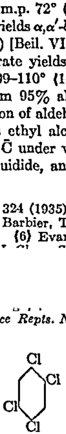
C̄ in alc. on refluxing with hydrazine hydrate yields (14) (15) o-chlorobenzhydrazide, white ndls. from alc., m.p. 117–118° (15), 109–110° (14). [This prod. with BzH yields benzal-o-chlorobenzhydrazide, white ndls. from 95% alc., m.p. 162° (15).] [For use of o-chlorobenzhydrazide as reagt. for identification of aldehydes and ketones see (15).]

C̄ on hydrolysis (Sap. Eq. = 184.5) yields ethyl alcohol (1:6130) + o-chlorobenzoic acid (3:4150). [For studies of hydrolysis of C̄ under various conditions see (7) (8) (12) (13) (3) (6).] — For the amide, anilide, p-toluidide, and other derivs. corresp. to C̄ see o-chlorobenzoic acid (3:4150).

3:6800 (1) Kohlrausch, Stockmair, *Monatsh.* **66**, 324 (1935). (2) Glutz, *Ann.* **143**, 196 (1867). (3) Kindler, *Ann.* **464**, 287 (1928). (4) Vavon, Barbier, Thiebaut, *Bull. soc. chim.* (5) **1**, 813 (1934). (5) Kekulé, *Ann.* **117**, 153–154 (1861). (6) Evans, Gordon, Watson, *J. Chem. Soc.* [illegible] (1915). (8) Cashmore, [illegible] rs, *Ann.* **422**, 166 (1921). [illegible] Settle, *J. Chem. Soc.* **121**, [illegible] **1926**, 2867. (14) Kalb, Gross, *Ber.* **59**, 732 (1926). (15) Sun, Sah, *Science Repts. Natl. Tsing Hua Univ.* A-2, 359–363 (1934); *Cent.* **1935**, I 57; *C.A.* **29**, 466 (1935).

—— 1,2,4,5-TETRACHLOROBENZENE

$C_6H_2Cl_4$ Beil. V - 205
V_1-(113)
V_2-(157)

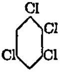


B.P. 243–246° cor. **M.P. 141°**

See 3:4115. *Division A: Solids.*

—— 1,2,3,5-TETRACHLOROBENZENE

$C_6H_2Cl_4$ Beil. V - 204
V_1-(113)
V_2-(157)

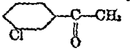


B.P. 246° cor. **M.P. 51°**

See 3:0915. *Division A: Solids.*

3:6815 *m*-CHLOROACETOPHENONE C_8H_7OCl Beil. S.N. 639

(*m*-Chlorophenyl methyl ketone)



B.P. 241–245° at 744 mm. (1) $D_4^0 = 1.2130$ (2)
227–229° (2)
127–131° at 30 mm. (3)
113° at 11 mm. (4)

Colorless liq. with aromatic odor. — Volatile with steam.

[For prepn. of $\bar{C}$ from *m*-chlorophenyl-phenyl-carbinol (2) by oxidn. with CrO_3/AcOH (90% yield) see (2); from *m*-aminoacetophenone [Beil. XIV-45, XIV_1-(365)] via diazotization and use of Cu_2Cl_2 reactn. (45% yield (4)) see (4) (3); from methyl *m*-chlorobenzoylacetate (2) by hydrolysis with 20% H_2SO_4 for 12 hrs. (65% yield) see (2).]

[For study of rate of reactn. with Br_2 see (4).]

$\bar{C}$ on htg. with 50% KOH as directed (1) gives 14% yield *m*-chlorobenzoic acid (3:4392).

Ⓓ *m*-Chloroacetophenone oxime: cryst. from AcOH, m.p. 88° (2) (1).

Ⓓ *m*-Chloroacetophenone *p*-nitrophenylhydrazone: maroon cryst. from AcOH, m.p. 175–176° (2). (The phenylhydrazone of $\bar{C}$ is unstable (2).)

Ⓓ *m*-Chloroacetophenone semicarbazone: cryst. from alc., m.p. 232° (3).

3:6815 (1) Lock, Böck, *Ber.* **70**, 920–921 (1937). (2) Wahl, Rolland, *Ann. chim.* (10) **10**, 29–30 (1928). (3) Edkins, Linnell, *Quart J Pharm. Pharmacol.* **9** 75–109; *Cent.* **1937**, I 4780; *C.A.* **30**, 6349 (1936). (4) Evans, Morgan, Watson, *J. Chem. Soc.* **1935**, 1172.

3:6825 *p*-CHLOROBENZOTRICHLORIDE $C_7H_4Cl_4$ Beil. V - 303
V_1—
V_2—

B.P. 245° (1)
99–100° at 4.9 mm. (2)

[For prepn. of $\bar{C}$ from *p*-hydroxybenzoic acid (1:0840) (3) (or the "*p*-hydroxybenzid" [Beil. X-154] obtd. from it by htg. (4)) with PCl_5 see indic. refs.; from *p*-toluenesulfonyl chloride [Beil. XI-103, XI_1-(26)] with Cl_2 at 150–200° see (5); from *p*-chlorotoluene (3:8287) with Cl_2 at high temp. in u v. light see (2); for formn. of $\bar{C}$ (together with other products) from benzotrichloride (3:6540) with Cl_2 under various circumstances see (1) (6) (7); for purification of $\bar{C}$ see (8).]

[For use of $\bar{C}$ with NaOAc in prepn. of acetic anhydride see (9); for use of $\bar{C}$ htd. with *p*-chlorobenzoic acid (3:4940) + $ZnCl_2$ + $FeCl_3$ in prepn. of *p*-chlorobenzoyl chloride (3:6550) see (10); for use of $\bar{C}$ with dichloroacetic acid (3 6208) + H_2SO_4 in prepn. of a mixt. of *p*-chlorobenzoyl chloride (3:6550) and dichloroacetyl chloride (3:5290) see (11).]

[For condens. of $\bar{C}$ with 1-hydroxynaphthoic acid-2 [Beil. X-331, X_1-(144)] in prepn. of dyestuff intermediates see (12); for react. of $\bar{C}$ with α-naphthol (1:1500) to yield 1-hydroxy-4-(*p*-chlorobenzoyl)naphthalene see (13).]

[$\bar{C}$ htd. with 99% HF (14) (15) or with $2SbF_3.NH_4HF_2$ at 150–160° (16) gives (86% yield (14)) *p*-chlorobenzotrifluoride, b.p. 137–138° (15).]

$\bar{C}$ on hydrolysis, e g., by htg. with aq. in s.t. at 200° (1), yields *p*-chlorobenzoic acid (3.4940) q v.

3:6825 (1) Beilstein, Kuhlberg, *Ann.* **150**, 295–296 (1869). (2) Maryott, Hobbs, Gross, *J. Am. Chem Soc.* **62**, 2321 (1940). (3) Anschütz, Moore, *Ann.* **239**, 346–348 (1887). (4) Klepl,

J. prakt. Chem. (2) **28**, 204–205 (1883). (5) Gilliard, Monnet, Cartier, Ger. 98,433, Dec. 12, 1896; *Cent.* **1898**, II 800. (6) Spreckels, *Ber.* **52**, 319 (1919). (7) Wertyporoch, *Ann.* **493**, 157–161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; *Cent.* **1931**, II 497; *C.A.* **25**, 3668 (1931). (9) Dr. A. Wacker Ges. für Elektrochem. Ind., Kaufler, Hormann, Brit. 165,747, June 30, 1921; *Cent.* **1922**, II 1218. (10) Scottish Dyes, Ltd., Bangham, Thomas, Brit. 308,231, April 18, 1929; *Cent.* **1929**, II 1348.

(11) Mills (to Dow Chem. Co.), U.S. 1,965,556, July 3, 1934; *Cent.* **1934**, II 2899; *C.A.* **28**, 5474 (1934). (12) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss 92,406, Feb. 16, 1923; *Cent.* **1923**, II 484. (13) Soc. Chem. Ind. Basel, Ger. 418,033, Aug. 26, 1925; *Cent.* **1925**, II 2095. (14) Osswald, Müller, Steinhauser (to I.G.), Ger. 575,593, May 22, 1933; *Cent.* **1933**, II 609. (15) I.G., French 745,293, May 8, 1933; *Cent.* **1933**, II 2061. (16) I.G., French 809,301, March 1, 1937; *Cent.* **1937**, I 4863; *C.A.* **31**, 6675 (1937).

3:6835 ω,ω-**DICHLOROACETOPHENONE** $C_8H_6OCl_2$ Beil. VII - 282

—CO.CHCl$_2$ VII$_1$-(152)

B.P.		M.P.	
245° at 760 mm.	(1)	20–21.5°	(7)
247–248° dec.	(2)	19°	(2)
249°	(3)	Not frozen at −10°	(1)
143° at 25 mm.	(2)		
142–144° at 25 mm.	(11)		
138–140° at 13 mm.	(5)		
132–134° at 13 mm.	(11)		
131–132° at 11 mm.	(6)		
128–129° at 14 mm.	(4)		
121–122° at 10 mm.	(1)		

Lachrymatory oil.

[For prepn. from acetophenone (1:5515) by actn. of Cl_2 (100% yield (4) (8)) in AcOH (80–94% yield (11)) see (4) (2) (11) or of sulfuryl chloride see (1); from phenylacetylene (1:7425) by actn. of HOCl (7), CH_3OCl (6), or C_2H_5OCl (5) see (7) (6) (5); from C_6H_6 + dichloroacetyl chloride (3:5290) (2) or dichloroacetonitrile (4) + $AlCl_3$ see (2) (4).]

$\bar{C}$ is almost unchanged by boiling with aq. (2). — $\bar{C}$ on shaking with 20 pts. 2 *N* aq. NaOH dissolves in 1–2 min.; after boiling under reflux for a few min. and acidifying, extraction with ether gives in 95% yield (8) 85–90% yield (11) *d,l*-mandelic ac. (1:0465), cryst. from $CHCl_3$ + pet. eth., m.p. 118.5° (8).

$\bar{C}$ on oxidn. with alk. $KMnO_4$ yields (1) (2) (3) (5) (6) benzoic ac. (1:0715), m.p. 121°. [$\bar{C}$ on treatment with NaOH + NaOCl in the cold yields benzoic ac. (1:0715) and chloroform in proportions depending upon conditions (9).] [Note that *d,l*-mandelic ac. (see above) may also be formed owing to actn. of alk. upon $\bar{C}$ cf. (9).]

$\bar{C}$ on nitration yields *m*-nitro-ω,ω-dichloroacetophenone, m.p. 57–58° (10).

$\bar{C}$ in alc. treated with excess alk. NH_2OH for 7–10 hrs. yields (6) phenylglyoxaldioxime [Beil. VII-672], cryst. from $CHCl_3$, m.p. 168° (6). [The product, m.p. 150–152°, so obtd. by (5) may have been a mixt. of the high-melting stereoisomer, m.p. 180°, with the low-melting stereoisomer, m.p. 168°.]

3:6835 (1) Durrans, *J. Chem. Soc.* **121**, 46 (1922). (2) Gautier, *Ann. chim.* (6) **14**, 345–347, 385–387 (1888). (3) Béhal, *Bull. soc. chim.* (2) **50**, 634 (1888). (4) Houben, Fischer, *Ber.* **64**, 2647–2648 (1931). (5) Goldschmidt, Endres, Dirsch, *Ber.* **58**, 575–576 (1925). (6) Jackson, *J. Am. Chem. Soc.* **56**, 977–978 (1934). (7) Wittorf, *J. Russ. Phys.-Chem. Soc.* **32**, 88–117 (1900); *Cent.* **1900**, II 30. (8) Houben, Fischer, *Ber.* **64**, 2644–2645 (1931). (9) Aston, Newkirk, Dorsky, Jenkins, *J. Am. Chem. Soc.* **64**, 1413–1416 (1942). (10) Rabcewicz-Zubkowski, *Roczniki Chem.* **9**, 532–537 (1929); *C.A.* **24**, 92 (1930).

(11) Aston, Newkirk, Jenkins, Dorsky, *Org. Syntheses* **23**, 48–51 (1943).

3:6840 3-CHLOROPROPANEDIOL-1,2 DIACETATE $C_7H_{11}O_4Cl$ Beil. II - 142
II_1-(67)
II_2—

(γ-Chloropropylene glycol diacetate, glycerol α-monochlorohydrin diacetate, "α-monochlorohydrin" diacetate)

CH_2Cl
|
HC—$OOCCH_3$
|
CH_2OOCCH_3

B.P.			
245°	at 740 mm.	(1)	
145–150°	at 40 mm.	(2)	
142–149°	at 40 mm.	(3)	
116°	at 12 mm.	(4)	
116–118°	at 11 mm.	(10)	
115–117°	at 10 mm.	(5)	
113–114°	at 9 mm.	(6)	
102–105°	at 6 mm.	(7)	
96.5–97°	at 0.4–0.6 mm.	(7)	
90–91°	at 0.8 mm.	(8)	

$D_4^{25} = 1.199$ (5) $n_D^{25} = 1.4386$ (5)

$n_D^{20} = 1.4407$ (8)

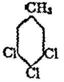
[For prepn. of C̄ from glycerol α-monochlorohydrin (3:9038) with Ac_2O (1:1015) (75% yield (6)) cf. (9) in pres. of a trace of H_2SO_4 (100% yield (4)) see indic. refs.; from epichlorohydrin (3:5358) with Ac_2O (1:1015) at 180° (1) (5) or in pres. of anhydrous $FeCl_3$ at ord. temp. (10) see indic. refs.; from 3-hydroxy-1,2-epoxypropane (glycidol) with large excess AcCl (3:7065) on htg. as directed (69% yield (7)) or from glyceryl-glycidol with AcCl (3:7065) at 60° for 2 hrs. (37% yield (8)) see indic. refs.]

[For prepn. of C̄ from glycerol (1:6540) with AcOH + HCl see (11); from glyceryl α,α′-diacetate with Ac_2O + HCl see (3); from glyceryl triacetate (triacetin) in dry ether at 0° with HCl gas (2) (3) cf. (4) see indic. refs.]

[C̄ in MeOH contg. 1% HCl at 60° for 6 hrs. gives (80% yield (8)) 3-chloropropanediol-1,2 (glycerol α-monochlorohydrin) (3:9038).]

3:6840 (1) Truchot, *Compt. rend.* **61**, 1170 (1865); *Ann.* **138**, 299 (1866). (2) de la Acena, *Compt. rend.* **139**, 868 (1904). (3) Seelig, *Ber.* **24**, 3469–3471 (1891). (4) Wegscheider, Zmerzlikar, *Monatsh.* **34**, 1068–1071 (1913). (5) Gibson, *J. Soc. Chem. Ind.* **50**, 949–954 (1931). (6) Nivière, *Compt. rend.* **156**, 1777 (1913); *Bull. soc. chim.* (4) **15**, 82–83 (1914). (7) Rider, *J. Am. Chem. Soc.* **54**, 775 (1932). (8) Sjöberg, *Svensk Kem. Tid.* **53**, 454–457 (1941); *Cent.* **1942**, II 25; *C.A.* **37**, 4363 (1943). (9) Abderhalden, Eichwald, *Ber.* **47**, 1859 (1914). (10) Knoevenagel, *Ann.* **402**, 135–136 (1914).
(11) Berthelot, de Luca, *Ann. chim.* (3) **52**, 461 (1858).)

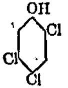
—— 3,4,5-TRICHLOROTOLUENE $C_7H_5Cl_3$ Beil. V - 209
V_1—
V_2—



B.P. 245.5–247° at 763 mm. M.P. 44.5–45.5°

See 3:0380. *Division A: Solids.*

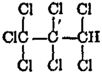
—— 2,4,5-TRICHLOROPHENOL $C_6H_3OCl_3$ Beil. VI—
VI$_1$—
VI$_2$-(180)



B.P. 244-248° at 746 mm. M.P. 67-68°

See 3:1620. *Division A: Solids.*

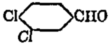
—— 1,1,1,2,2,3,3-HEPTACHLOROPROPANE C_3HCl_7 Beil. I - 108
I$_1$-(35)
I$_2$-(73)



B.P. 247-248° sl. dec. M.P. 29-30° D_4^{24} = 1.8043

See 3:0200. *Division A: Solids.*

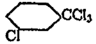
—— 3,4-DICHLOROBENZALDEHYDE $C_7H_4OCl_2$ Beil. VII - 238
VII$_1$-(134)



B.P. 247-248° M.P. 43-44°

See 3:0550. *Division A: Solids.*

3:0845 *m*-CHLOROBENZOTRICHLORIDE $C_7H_4Cl_4$ Beil. V -303
V$_1$—
V$_2$—



B.P. 247-250° (1)

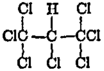
[For prepn. from *m*-hydroxybenzoic acid (1:0825) (1) or from *m*-sulfobenzoic acid [Beil. XI-384, XI$_1$-(98)] (2) with PCl_5 see indic. refs.; for studies on formn. of C̄ from benzotrichloride (3:6540) with Cl_2 see (3) (4); for purification of C̄ see (5).]

[For condens. of C̄ with 1-hydroxynaphthoic acid-2 [Beil. X-331, XI$_1$-(144)] in prepn. of dyestuff intermediates see (6).]

C̄ on hydrolysis presumably yields *m*-chlorobenzoic acid (3:4392) q.v.

3:0845 (1) Anschütz, Moore, *Ann.* 239, 342 (1887). (2) Kämmerer, Carius, *Ann.* 131, 158 [illegible] (4) Spreckels, *Ber.* 52, 319 (1919). [illegible] 931; *Cent.* 1931, II 497; *C.A.* 25, 3668 [illegible] 1922; Swiss, 92,406, Feb. 16, 1923; *Cent.* 1923, II 484.

3:0860 1,1,1,2,3,3,3-HEPTACHLOROPROPANE C_3HCl_7 Beil. I —
(*sym.*-Heptachloropropane) I$_1$-(35)
I$_2$—



B.P.		M.P.
249°	(1)	11-11.5° (1) D_4^{24} = 1.7921 (1) n_D^{21} = 1.5427 (1)
105° at 90 mm.	(1)	
[illegible]-132° at 20 mm.	(2)	

Oil with disagreeable odor.

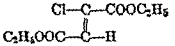
[For prepn. from trichloroethylene (3:5170) + CCl_4 + $AlCl_3$ (49% yield (2)) by stdg. 48 hrs. at 20–30° (2) see (2) (1).]

$\bar{C}$ dislvd. in CCl_4 and heated at 60–70° with $AlCl_3$ evolves HCl and gives (83% yield (3)) hexachloropropene (3:6370).

$\bar{C}$ in alc. on titration with alk. gives (3) an apparent Neut. Eq. of 285.5 by loss of 1 HCl and formation of hexachloropropene (3:6370).

3:6860 (1) Prins, *J. prakt. Chem.* (2) 89, 417 (1914). (2) Henne, Ladd, *J. Am. Chem. Soc.* 60, 2494–2495 (1938). (3) Prins, *Rec. trav. chim.* 54, 251 (1935).

3:6864 DIETHYL CHLOROFUMARATE $C_8H_{11}O_4Cl$ Beil. II - 745 II_1-(302) II_2-(640)



B.P.						
250°	at 760 mm., sl. dec.	(1)	$D_-^{24} = 1.19517$	(7)	$n_D^{24} = 1.4598$	(7)
243–245° u.c.	at 735 mm.	(10)				
202–203°	at 210 mm.	(1)	$D_4^{20} = 1.188$	(8)	$n_D^{20} = 1.4571$	(8)
136.5° cor.	at 19 mm.	(2)	1.187	(8)	1.4564	(8)
135–136°	at 17 mm.	(8)	1.183	(4)		
127°	at 10 mm.	(3)				
119°	at 12 mm.	(4)	$D_4^{18.3} = 1.1890$	(8)	$n_D^{18.3} = 1.45782$	(8)
117°	at 7 mm.	(5)				
108°	at 16 mm.	(6)	$D_4^{18.2} = 1.1903$	(8)	$n_D^{18.2} = 1.45723$	(8)
			$D_4^{16.3} = 1.1822$	(4)	$n_{He}^{16.3} = 1.45979$	(4)

[*See also diethyl chloromaleate* (3:6697).]

Colorless liq with irritating actn. on skin and whose vapor strongly attacks the eyes. — Insol. cold aq., eas. sol. alc., ether; volatile with steam.

[For prepn. of $\bar{C}$ from chlorofumaric acid (3:4853) in abs. EtOH with HCl gas (1) or conc. H_2SO_4 (4) see indic. refs.; from chlorofumaryl (di)chloride (3:6105) with EtOH see (10) (1) (9) (3).]

[For formn. of $\bar{C}$ from diethyl *d*-tartrate (1:4256) with PCl_5 see (11) (note that ethyl hydrogen chlorofumarate, cryst. from pet. ether, m.p. 52–53°, has also been obtd. (12) as *one of the prods. of this reactn.); from diethyl d,l(?)-α,α-dichlorosuccinate by loss of* HCl under actn. of dimethylaniline see (5).]

[$\bar{C}$ (1 mole) with diethyl sodio-malonate (1 mole) is said (13) to yield tetraethyl cyclopropane-1,1,2,3-tetracarboxylate [Beil. IX-991] although no details are given; in the presence of excess NaOEt in cold alc. for 12 hrs., however, the same components give (15–20% yield (14)) (15) triethyl γ-carbethoxyaconitate [Beil. II-876], b.p. 205–207° at 16 mm. (14); for reactn. of $\bar{C}$ (1 mole) with diethyl mono- and di-substituted malonates yielding triethyl corresp. subst. aconitates see (13) — $\bar{C}$ (1 mole) with ethyl *sodioaceto-acetate* (1 mole) in abs. alc. refluxed for ½ hr. gives (72% yield (3)) (16) triethyl γ-acetyl-*aconitate [Beil. III-860], yel. oil, b.p. 187–188° at 15 mm. (3),* the same as similarly obtd. (3) from diethyl chloromaleate (3:6697).]

[$\bar{C}$ *with o-chlorophenol (3:5980)* or its Na deriv. in boilg. xylene for 2 hrs. gives (77% yield (17)) diethyl o-chlorophenoxyfumarate, b.p. 203–204° at 14 mm. (17). — $\bar{C}$ with *p*-chlorophenol (3:0475) + NaOEt gives (17) diethyl p-chlorophenoxyfumarate, b.p. 199–200° at 12 mm. (17).]

The reactn. of $\bar{C}$ with NH_3 under various circumstances is disputed and confused and cannot profitably be discussed here; for refs. see Beil. II-745.

$\bar{C}$ (1 mole) with hydrazine hydrate (2 moles) directly (18) or in alc. or AcOH (9) yields ethyl pyrazolone-5 (or 3)-carboxylate-3 (or 5) [Beil. XXV-206, XXV_1-(567)], ndls. from boilg. aq., m.p. 184–185° (18); 178° (9); note that in the direct treatment with just 2 moles of hydrazine hydrate much heat is evolved and the product ppts. on cooling; if excess base is employed (in which the prod. is soluble) neutralization with acid is necessary.

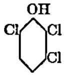
[$\bar{C}$ with phenylhydrazine reacts much more slowly; however, after several hrs. at 100° phenylhydrazine HCl ppts. leaving an oil from which a cryst. prod. spar. sol. in boilg. AcOH but sepg. from it in colorless ndls., m.p. 272° dec., can be obtd. (18); this prod. is *not*, however, the ethyl 1-phenylpyrazolone-5(or 3)-carboxylate-3(or 5) which might be expected, but is regarded [Beil. XXVI-578] (18) as a 4,4′-*bis* derivative of it.

$\bar{C}$ on boilg. with 1:1 HCl and subsequent evapn. to dryness undergoes hydrolysis yielding (4) chlorofumaric acid (3:4853), m.p. 191.5° (4).

3:6864 (1) Perkin, *J. Chem. Soc.* **53**, 700–703 (1888). (2) Walden, Swinne, *Z. physik. Chem.* **79**, 742 (1912). (3) Ruhemann, Tyler, *J. Chem. Soc.* **69**, 532–535 (1896). (4) von Auwers, Harres, *Ber.* **62**, 1679, 1685–1687 (1929). (5) Darzens, Sejourne, *Compt. rend.* **154**, 1617 (1912). (6) von Auwers, Harres, *Z. physik. Chem.* **A-143**, 10 (1929). (7) Gladstone, *J. Chem. Soc.* **59**, 293 (1891). (8) von Auwers, Schmidt, *Ber.* **46**, 481 (1913). (9) Ruggli, Hartmann, *Helv. Chim. Acta* **3**, 513 (1920). (10) Claus, *Ann.* **191**, 80–93 (1878).

(11) Henry, *Ann.* **156**, 178–179 (1870). (12) Patterson, Todd, *J. Chem. Soc.* **1929**, 1768–1770. (13) Ruhemann, *J. Chem. Soc.* **81**, 1212–1214 (1902). (14) Desai, *J. Chem. Soc.* **1932**, 1089–1090. (15) Bland, Thorpe, *Proc. Chem. Soc.* **28**, 131 (1912). (16) Ruhemann, *J. Chem. Soc.* **71**, 323–324 (1897). (17) Ruhemann, *Ber.* **54**, 916–918 (1921). (18) Ruhemann, *J. Chem. Soc.* **69**, 1394–1397 (1896).

—— **2,3,6-TRICHLOROPHENOL**

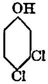


$C_6H_3OCl_3$ Beil. VI - 190, VI_1—, VI_2-(180)

B.P. 252–253° u.c. **M.P. 58°**

See 3:1160. *Division A: Solids.*

—— **3,4-DICHLOROPHENOL**



Beil. VI - 190, VI_1-(103), VI_2-(179)

B.P. 253.5° at 767 mm. **M.P. 65°**

See 3:1460. *Division A: Solids.*

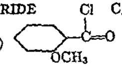
—— **1,2,3,4-TETRACHLOROBENZENE**

$C_6H_2Cl_4$ Beil. V - 204, V_1—, V_2-(156)

B.P. 254° cor. at 761 mm. **M.P. 45–46°**

See 3:0655. *Division A: Solids.*

3:6870 2-METHOXYBENZOYL CHLORIDE $C_8H_7O_2Cl$ Beil. X - 85
(o-Anisoyl chloride; X_1-(43)
salicyloyl chloride methyl ether)



B.P.	254° u.c.	at 760 mm.	(1)
	133°	at 19 mm.	(2)
	145° cor.	at 17 mm.	(3)
	136°	at 12 mm.	(4)
	128°	at 11 mm.	(5)
	128.8–129.0°	at 8 mm.	(6)
	119.6°	at 1 mm.	(7)
	105–106°	at 1 mm.	(8)

Colorless liquid.

[For prepn. of C̄ from o-methoxybenzoic acid (o-anisic acid) (1:0685) with PCl_5 (1) (4) (9) (10) (11) (every trace of salicylic acid must first be removed (9)) or with $SOCl_2$ (2) (3) (4) (5) (6) (7) (12) (prolonged heating tends to demethylate product (4)) see indic. refs.; note that for none of the prepns. is the yield recorded.]

[C̄ on cat. reductn. at 280° with H_2 at ord. press. in pres. of Pd gives (11), not the expected o-methoxybenzaldehyde, but instead o-methoxytoluene (methyl o-tolyl ether) (1:7480).]

C̄ with anhydrous Na_2CO_3 in pyridine shaken for ½ hr., poured onto ice, yields (13) o-methoxybenzoic acid anhydride, ndls. from pet ether, m.p. 72.4° (13).

[C̄ with C_6H_6 + $AlCl_3$ gives (14) (9) (2) (12) o-hydroxybenzophenone (1:1414) (note demethylation of intermediate o-methoxybenzophenone (1·5142) and also the formn. in small amt. (12) of 2-hydroxy-5-(2′-hydroxybenzoyl)benzophenone, m.p. 131–132° (12)).]

[C̄ with Et_2Zn gives (87% yield (3)) ethyl 2-methoxyphenyl ketone [Beil. VIII-102], b.p. 137° cor. at 16 mm. (3).]

[For reaction of C̄ with ethyl sodio-acetoacetate (5), with ethyl sodio-α-methylacetoacetate (15), with ethyl sodio-α-allylacetoacetate (16), or with ethyl sodio-α,γ-dimethoxyacetoacetate (17) (together with hydrolytic cleavage of the resulting products to ketones and/or acids) see indic. refs.; for reactn. of C̄ with Na phenylacetylene and ring closure of intermediate to corresp. 2-methoxyflavone see (18).]

[C̄ (1 mole) with HCN (4 moles) in dry ether + pyridine gives (4) o-methoxybenzoyl cyanide, yel. ndls. from lgr., m.p. 56°, b.p. 161° at 12 mm. (4).]

[C̄ with urea refluxed in C_6H_6 for 15 hrs. gives (19) N-(o-methoxybenzoyl)urea, ndls. from hot aq. or toluene, m.p. 192° (19).]

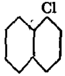
[C̄ with methyl salicylate gives (20) methyl O-(2-methoxybenzoyl)salicylate, m.p. 102–104° (20); C̄ with salicylamide in pyridine gives (21) N-(2-methoxybenzoyl)salicylamide, m.p. 189° (21).]

[C̄ with MeOH yields methyl o-methoxybenzoate (1:4091), b.p. 248°; C̄ with EtOH yields ethyl o-methoxybenzoate (1:4151), b.p. 261°; for study of rate of reactn. of C̄ with EtOH at 0° see (22) (8).]

C̄ on hydrolysis yields o-methoxybenzoic acid (1:0685), m.p. 100–101°; for the amide, anilide, and other derivs. corresp. to C̄ see o-methoxybenzoic acid (1:0685).

3:6870 (1) Pinnow, Müller, *Ber.* 28, 158 (1895). (2) Staudinger, Kon, *Ann.* 384, 99 (1911). (3) Fischer, Slimmer ...
(1925). (5) von A ...
B-38, 136 (1938). ...
J. Am. Chem. Soc. ...
Cohen, Dudley, *J.* ...

3:6878 1-CHLORONAPHTHALENE $C_{10}H_7Cl$ Beil. V - 541
V_1-(262)
V_2-(444)



B.P.			F.P.		
[263°		(1)]	−2.3°	(9)	D_4^{25} = 1.192 (6)
[259–262°		(2)]	−2.5°	(6)	
259.4–260.3°	at 760 mm.	(3)	−4°	(12)	$D_4^{21.6}$ = 1.1906 (7)
259.3°	at 760 mm.	(4) (5)			
258.8°	at 753 mm.	(6)			$n_D^{21.6}$ = 1.63184 (7)
258° cor.		(7)			
255.5–256.0°		(8)			D_4^{20} = 1.19382 (4)
255.6° cor.	at 752 mm.	(9)			1.192 (7)
248.6°	at 600 mm.	(4)			
230.8°	at 400 mm.	(4)			n_D^{20} = 1.63321 (4) (7)
204.2°	at 200 mm.	(4)			
180.4°	at 100 mm.	(4)			D_{15}^{15} = 1.1966 (9)
171.4°	at 75 mm.	(4)			
159.3°	at 50 mm.	(4)			
144.0–146.5°	at 29 mm.	(10)			
140.3°	at 25 mm.	(4)			
129.54°	at 16 mm.	(5)			
125.4°	at 16 mm.	(11)			
127.97°	at 15 mm.	(5)			
126.25°	at 14 mm.	(5)			
122.0–122.2°	at 13 mm.	(3)			
118.6°	at 10 mm.	(4)			
104.8°	at 5 mm.	(4)			
85.3°	at 1.5 mm.	(4)			

Colorless oil, volatile with steam. — Note that presence of as much as 10% of 2-chloronaphthalene (3:1285) has no effect upon density of $\bar{C}$ (9). — Note also that addn. of 1,4-dichloronaphthalene (3:1655), m.p. 68°, or of 1,6-dichloronaphthalene (3:0810), m.p. 48°, lowers m.p. of $\bar{C}$ (9).

[For sepn. of mixts. of $\bar{C}$ with the isomeric 2-chloronaphthalene by fractional freezing of their soln. in appropriate solvents see (6). — For purification of tech. $\bar{C}$ by treatment with 1–2% alk. at 150° under reduced press. see (13). — For sepn. of $\bar{C}$ from dichloronaphthalenes by means of its const.-boil. mixt. (b.p. 99°) with aq. see (18).]

[For prepn. of $\bar{C}$ from α-naphthylamine [Beil. XII-1212, XII_1-(519)] via diazotization and use of Cu_2Cl_2 reactn. (70–75% yield (9)) (8) (7) or even by warming diazo soln. with HCl (10–20% yield (14)) or from diazonium/$ZnCl_2$ cpd. on addn. to phenol at 60° (46% $\bar{C}$ + 29% hydroxybiphenyl + 20% diphenyl ether (62)) see indic. refs.; from α-naphthalenesulfonyl chloride [Beil. XI-157, XI_1-(37)] (2), or from 1-nitronaphthalene [Beil. V-553, V_1-(264)] (15), or from β-naphthol (1:1500) (16) with PCl_5 as directed see indic. refs.; for formn. of $\bar{C}$ from 1-nitronaphthalene with Cl_2 see (17).]

[For prepn. of $\bar{C}$ from naphthalene with Cl_2 in boilg. naphthalene (19) (48), in vapor phase (20) (22) (27), in various solvents (21) (22) (23) (24) (25) (26) see indic. refs.; from naphthalene with HCl gas + air in pres. of cat. see (28); from naphthalene with $PbCl_4 \cdot 2NH_4Cl$ at 140–150° (29) or with SO_2Cl_2 + $AlCl_3$ (79% yield (30)) see indic. refs.; from

naphthalene dichloride [Beil. V-519] with boilg. alc. KOH (31) cf. (32) or by distn. (33) cf. (34) see indic. refs.]

[For thermal anal. of systems of $\bar{C}$ with $SbBr_5$ see (35); with PkOH see (36); with 2,4,6-trinitroresorcinol (styphnic acid) see (37).]

[$\bar{C}$ with Cl_2 in cold or $\bar{C}$ with Cl_2 in lt. pet. yields (38) 1-chloronaphthalene tetrachloride, m.p. 131° (38), and 1,4-dichloronaphthalene (3.1655), m.p. 68° (38); $\bar{C}$ with Cl_2 in $CHCl_3$ yields (38) the above 1-chloronaphthalene tetrachloride and 1,4-dichloronaphthalene tetrachloride, m.p. 172° (38); $\bar{C}$ with Cl_2 in CS_2 gives (38) a new dichloronaphthalene tetrachloride, m.p. 158° (38).]

[$\bar{C}$ on chloromethylation with paraformaldehyde + HCl gas + H_3PO_4 in AcOH gives (81) 1-chloro-4-(chloromethyl)naphthalene, m.p. 78–79° (81).]

[$\bar{C}$ is *not* reduced with excess 5% Na/Hg in alc. even after 5 hrs. (39) nor by HI + P at 182° for 10 hrs. (42); however, $\bar{C}$ in boilg. AmOH treated with Na yields (40) 1,4-dihydronaphthalene [Beil. V-518, V_1-(249)] (identified by addn. of Br_2 giving dibromide, m.p. 74° (40)) and 1,2,3,4-tetrahydronaphthalene (1:7550) q.v.; furthermore, $\bar{C}$ with Mg in boilg. MeOH evolves gas and upon acidification and pouring into aq. gives alm. quant. yield (41) naphthalene (1:7200), m.p. 80°.]

[$\bar{C}$ on cat. oxidn. with air at 250–300° gives (43) 97% phthalic anhydride (1:0725) + 3% 3-chlorophthalic anhydride (3:3900).]

[$\bar{C}$ with Li in s.t. 17½ hrs. at 263° followed by treatment with aq. gives (44) naphthalene (1:7200) + 1,1′-binaphthyl [Beil. V-725, V_1-(358)], m.p. 156°. — $\bar{C}$ with Li in dry ether yields soln. of α-naphthyl-lithium which with Me_2SO_4 gives (77% yield (45)) 1-methylnaphthalene (1:7600), the reactn. of $\bar{C}$ with Li occurring even more readily (46) than with Mg.]

[$\bar{C}$ with Mg at 200–220° reacts very energetically and is complete within a few minutes; naphthalene sublimes abundantly, and yield of α-$C_{10}H_7MgCl$ is only 10–13% (47).]

[$\bar{C}$ with $AlCl_3$ at 100° gives small amts. (50) naphthalene (1:7200) + 2-chloronaphthalene (3:1285).]

[$\bar{C}$ with CuCN in pyridine htd. 24 hrs. in bath at 245–250° (92% yield (10)) or $\bar{C}$ with $K_4Fe(CN)_6$ + pyridine at 270° for 18 hrs. (49) gives α-naphthonitrile [Beil. IX-649, IX_1-(275)], b.p. 299° cor., b.p. 173–174° at 27 mm., 166–169° at 18 mm. (10).]

[$\bar{C}$ does *not* with Ag 3,5-dinitrobenzoate yield corresp. ester (80).]

[$\bar{C}$ with 15% aq. NaOH above 300° for 12 hrs gives (46% yield (51)) α-naphthol (1:1500); $\bar{C}$ with 5 moles 3–25% aq. NaOH at 350–360° under pressure in pres. of Cu for 1 hr. gives (52) a mixt. of α-naphthol (1:1500) + β-naphthol (1:1540). — $\bar{C}$ with aq. Na_2CO_3 + Cu at 300° under press. (53) or $\bar{C}$ with aq. Na_2CO_3, Na_2HPO_4, or $Na_2B_4O_7$ at 325° and 280 atm. (54) yields α-naphthol (1:1500). — $\bar{C}$ with aq. vapor over cat. at 300–400° yields (55) α-naphthol (1:1500).]

[$\bar{C}$ with conc. aq. NH_4OH + CuO at 150–250° under press. (56) or $\bar{C}$ with conc. aq. NH_4OH + Cu_2Cl_2 + $Ca(OH)_2$ at 225–230° under press. (57) cf. (58) yields α-naphthylamine (for study rate of reactn. see (58) (61); under suitable conditions the main prod. may be di-α-naphthylamine (60).]

[$\bar{C}$ with KNH_2 in liq. NH_3 at −33° gives (82) only 2–3% α-naphthylamine, the main prod. (43–53%) being β-naphthylamine; for behavior of $\bar{C}$ with $LiNEt_2$ see (83).]

[$\bar{C}$ on mononitration, e.g., with a mixt. of conc. HNO_3 (D = 1.4) (1 mole) + conc. H_2SO_4 (2 moles) at 0° (63) cf. (64) (65) (66) gives a mixt. of *three* mono nitro derivs., viz., 1-chloro-4-nitronaphthalene [Beil V-555, V_1-(264)], pale yel. ndls. from alc., m.p. 85° (66) (63), 87–87.5° (67); 1-chloro-5-nitronaphthalene [Beil. V-556], m.p. 111° (63) (68); and 1-chloro-8-nitronaphthalene [Beil. V-556], ndls. from AcOH or C_6H_6, m.p. 94° (63), 93–94° (69). (Note that the relative proportions of these three *mononitration* products

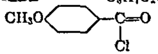
[C̄ on htg. with Cu powder in C_6H_6 for 25 hrs. gives (5) a mixt. of the two stereoisomeric forms of 1,2-*bis*-(o-chlorophenyl)-1,2-dichloroethylene, [Beil. V-635]; by repeated cryst. from pet. ether this mixt. is separable into 3 pts. higher-melting stereoisomer, m.p. 172° (5), and 1 pt. lower-melting stereoisomer, m.p. 129° (5).]

C̄ on hydrolysis, e.g., by htg. with aq. in s.t. at 150° (1) or by boilg. with conc. HNO_3 (2), yields *o*-chlorobenzoic acid (3:4150) q.v.

3:6880 (1) Kolbe, Lautemann, *Ann.* **115**, 183–185, 195–196 (1860). (2) Anschütz, *Ann.* **454**, 95–99 (1927). (3) Meister Lucius Brüning, Ger. 229,873, Jan. 6, 1911, *Cent.* **1911**, I 358. (4) Anschütz, Moore, *Ann.* **239**, 321–322 (1887). (5) Fox, *Ber.* **26**, 653–656 (1893). (6) Spreckels, *Ber.* **52**, 319 (1919). (7) Wertyporoch, *Ann.* **493**, 157–161 (1932). (8) Britton (to Dow Chem. Co.), U.S. 1,804,458, May 12, 1931; *Cent.* **1931**, II 497; *C.A.* **25**, 3668 (1931). (9) Kyrides (to Nat. Aniline and Chem. Co.), U.S. 1,733,268, Oct. 29, 1929; *Cent.* **1930**, I 3831. (10) Soc. Chem. Ind. Basel, Ger. 355,115, June 21, 1922; Swiss, 92,406, Feb. 16, 1923; *Cent.* **1923**, II 484.

(11) Soc. Chem. Ind. Basel, Ger. 378,908, Aug. 7, 1923; Ger. 378,909, Aug. 11, 1923; Swiss 98,559, April 2, 1923; *Cent.* **1923**, IV 593. (12) Soc. Chem. Ind. Basel, Ger. 418,033, Aug. 26, 1925; *Cent.* **1925**, II 2095. (13) Scottish Dyes, Ltd., Bangam, Thomas, Brit. 308,231, April 18, 1929; *Cent.* **1929**, II 1348. (14) I.G., French 745,293, May 8, 1933; *Cent.* **1933**, II 2061.

3:6890 4-METHOXYBENZOYL CHLORIDE $C_8H_7O_2Cl$ Beil. X - 163
(*p*-Anisoyl chloride) X_1-(77)



B.P.			M.P.		
262–263° sl. dec.		(1)	24°	(7)	$D_4^{20} = 1.2609$ (6) $n_D^{20} = 1.5802$ (6)
262°		(9)	22° (4)	(15)	
258.4–260.5°		(2)	21°	(8)	
161–168°	at 38 mm.	(3)			
160–164°	at 35 mm.	(4)			
152–153°	at 24 mm.	(4)			
148–153°	at 20 mm.	(5)			
145°	at 14 mm.	(4)			
137.6–137.8°	at 14 mm.	(2)			
90.8°	at 1 mm.	(6)			

[For prepn. of C̄ from *p*-methoxybenzoic acid (*p*-anisic acid) (1:0805) with PCl_5 (93% yield (3)) (4) (9) (10) (11) or with $SOCl_2$ (6) (7) (12) (13) see indic. refs.; from sodium *p*-anisate with oxalyl chloride (3:5060) in C_6H_6(75–90% yield) see (14).]

[C̄ with 3% H_2O_2 in acetone + pyridine at 0° yields (15) di-*p*-anisyl peroxide, cryst. from AcOEt or pet. eth., m.p. 128° (15); for reactn. of C̄ with H_2S_2 + $ZnCl_2$ giving (60% yield) di-*p*-anisyl disulfide see (30).]

[C̄ on cat. reductn. with H_2 and cat. as directed gives (81% yield (16)) *p*-methoxybenzaldehyde (1:0240) (under some conds. (17) reductn. goes to *p*-methoxytoluene (methyl-*p*-tolyl ether) (1:7495)).]

[Although 2-methoxybenzoyl chloride (3:6870) with anhydrous Na_2CO_3 + pyridine gives the corresp. anhydride, this reactn. is not specifically reported for C̄; however, C̄ + a tertiary amine (pyridine) in C_6H_6 with excess $K_2S_2O_5$ yields (18) *p*-methoxybenzoic acid anhydride, m.p. 99–100° (18).]

[C̄ with C_6H_6 + $AlCl_3$ yields (1) *p*-methoxybenzophenone (1:5170); C̄ with toluene + $AlCl_3$ gives (40% yield (11)) 4-methoxy-4′-methylbenzophenone, cryst. from alc., m.p. 89° (11); C̄ with perylene + $AlCl_3$ in CS_2 gives (19) 3,9-*bis*-(*p*-methoxybenzoyl)perylene, m.p. 319.5° (19).]

[C̄ condenses with many phenol ethers in pres. of $AlCl_3$; e.g., for reactn. of C̄ with anisole

yielding 4,4′-dimethoxybenzophenone [Beil. VIII-317, VIII$_1$-(641)], m.p. 143–144° (20), see (20) (21); for C̄ with phenetole yielding 4-methoxy-4′-ethoxybenzophenone, m.p. 112° (13), 111° (20), *see indic. refs.*; for C̄ with pyrocatechol dimethyl ether (veratrole) (1:7560) yielding 3,4,4′-trimethoxybenzophenone [Beil. VIII-422], m.p. 98–99°, see (22); for C̄ with resorcinol dimethyl ether (1:7570) yielding 2,4,4′-trimethoxybenzophenone [Beil. VIII$_1$-(702)], m.p. 70–71° (23), see (23); for C̄ with phloroglucinol trimethyl ether (1:7148) yielding 2,4,6,4′-tetramethoxybenzophenone [Beil. VIII-496], m.p. 146°, see (22); for C̄ with many other phenol ethers see (20).]

[C̄ with MeZnI (24) or better with Me_2Cd (25) gives (yields. 25% (24), 84% (25)) *p*-methoxyphenyl methyl ketone (*p*-methoxyacetophenone) (1.5140), m.p. 38°; C̄ with C_6H_5ZnBr gives (65% yield (26)) *p*-methoxybenzophenone, (1:5170), m.p. 61°, b.p. 202° at 14 mm. (26)]

[C̄ with ethyl sodioacetoacetate yields (4) ethyl α-(*p*-methoxybenzoyl)acetoacetate [Beil. X-1004]; C̄ with ethyl sodio-α,γ-dimethoxyacetoacetate yields (27) ethyl α,γ-dimethoxy-α-(*p*-anisoyl)acetoacetate (which on ketonic hydrolytic cleavage yields (27) ω,4-dimethoxyacetophenone).]

[C̄ (1 mole) with HCN (4 moles) in dry ether + pyridine gives (12) *p*-methoxybenzoyl cyanide, m.p. 63°, b.p. 150° at 12 mm. (12); C̄ with KCN + quinoline yields (28) 1-(*p*-anisoyl)-2-cyano-1,2-dihydroquinoline, m.p. 120°, which upon acid hydrolysis gives (57% yield (28)) *p-methoxybenzaldehyde (p-anisaldehyde) (1:0240).*]

[C̄ with urea refluxed in C_6H_6 for 15 hrs. yields (29) *N*-(*p*-methoxybenzoyl)urea, ndls. from alc., m.p. 215° (29).]

[*For reactn. of C̄ with K_2S in alc. + ether yielding* K salt of *p-methoxythiobenzoic acid* see (30); for reactn. of C̄ with sodium phenylacetylene see (31); for reactn. of C̄ with diphenylketene see (32); for reactn. of C̄ with *d*-glucose and other carbohydrates see (33); for reactn. of C̄ *with* 3,4-dimethoxyphenylethylamine (34) *or with* β-(*n*-butylamino)ethanol (3) see indic. refs.]

C̄ with MeOH yields methyl *p*-methoxybenzoate (methyl *p*-anisate) (1:2128), m.p. 49°; C̄ with EtOH yields ethyl *p*-anisate (1:4191), b.p. 269°, m.p. +7° (for study of rate of reactn. of C̄ with EtOH see (8) (35)).

C̄ on hydrolysis yields *p*-methoxybenzoic acid (1·0805), m.p. 184°; for the amide, anilide, *p*-toluidide, and other derivs. corresp. to C̄ see *p*-methoxybenzoic acid (1:0805).

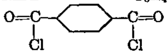
3:6890 (1) Ullmann, Goldberg, *Ber.* **35**, 2814 (1902). (2) Kohlrausch, Pongratz, Stockmair *Monatsh.* **67**, 110 (1935). (3) Pierce, Salsbury, Fredericksen, *J. Am. Chem. Soc.* **64**, 1691–1694 (1942). (4) Schoonjans, *Bull. acad. roy. Belg.* (3) **33**, 810–820 (1897), *Cent.* **1897**, II 616. (5) de Ceuster, *Natuurw. Tijdschr.* **14**, *Nos.* 3–6, 188–202 (1932), *Cent.* **1932**, II 1290. (6) Thompson, Norris, *J. Am. Chem. Soc.* **58**, 1956 (1936). (7) Meyer, *Monatsh.* **22**, 428 (1901). (8) Branch, Nixon, *J. Am. Chem. Soc.* **58**, 2499–2504 (1936). (9) Cahours, *Ann. chim.* (3) **23**, 350–354 (1848); *Ann.* **70**, 47–48 (1849). (10) Lossen, *Ann.* **175**, 284, Note (1875).

(11) Orechow, Brouty, *Bull. soc. chim.* (4) **47**, 623 (1930). (12) Marsh, Stephen, *J. Chem. Soc.* **127**, 1635 (1925). (13) Schönberg, Schütz, Nickel, *Ber.* **61**, 1380 (1927). (14) Adams, Uhlich, *J. Am. Chem. Soc.* **42**, 606 (1920). (15) Vanino, Uhlfelder, *Ber.* **37**, 3624 (1904). (16) Rosenmund, Zetsche, *Ber.* **56**, 1483 (1923). (17) Rosenmund, Zetsche, *Ber.* **54**, 641 (1921). (18) Gasopoulos, *Praktika Akad. Athenon* **6**, 347–353 (1931); *Cent.* **1932**, I 3172. (19) Zinke, Funke, *Ber.* **58**, 2225 (1925). (20) Jones, *J. Chem. Soc.* **1936**, 1860.

(21) Schnackenberg, Schell, *Ber.* **36**, 654 (1903). (22) von Kostanecki, Tambor, *Ber.* **39**, 4024, 4026 (1906). (23) Ziegler, Ochs, *Ber.* **55**, 2273 (1922). (24) Mauthner, *J. prakt. Chem.* (2) **103**, 392, 396 (1922). (25) Gilman, Nelson, *Rec. trav. chim.* **55**, 528–529 (1936). (26) Martynoff, *Ann. chim.* (11) **7**, 439 (1937). (27) Pratt, Robinson, *J. Chem. Soc.* **127**, 169 (1925). (28) Sugasawa, Tsuda, *J. Pharm. Soc. Japan*, **56**, 103–105 (1936); *Cent.* **1936**, II 3670. (29) Kaufmann, *Arch. Pharm.* **265**, 236 (1927). (30) Block, Bergmann, *Ber.* **53**, 974–975 (1920).

(31) Weygand, Bauer, *Ann.* **459**, 141 (1927). (32) Staudinger, Kon, *Ann.* **384**, 117 (1911). (3) Oden, *Arkiv Kemi, Mineral. Geol.* **7**, *No.* 16, 1–16 (1918), *Cent.* **1923**, III 254–256; *C.A.* **14**, 2171 (1920). (34) Ahluwalia, Narang, Ray, *J. Chem. Soc.* **1931**, 2058. (35) Norris, Fasce, Staud, *J. Am. Chem. Soc.* **57**, 1415–1420 (1935).

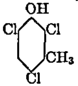
— TEREPHTHALYL (DI)CHLORIDE $C_8H_4O_2Cl_2$ Beil. IX_1- 844 IX_1-(376)



B.P. 263° **M.P. 83°**

See 3:2205. *Division A: Solids.*

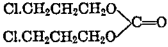
— 2,4,6-TRICHLORO-3-METHYLPHENOL $C_7H_5OCl_3$ Beil. VI — VI_1— VI_2-(356)



B.P. 265° **M.P. 46°**

See 3:0618. *Division A: Solids.*

3:6895 DI-(γ-CHLOROPROPYL) CARBONATE $C_7H_{12}O_3Cl_2$ Beil. III — III_1— III_2-(5)
(γ,γ-Dichloropropyl carbonate)

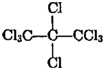


B.P. 265–270° at 740 mm. (1)

[Obtd. as by-product in prepn. of γ-chloropropyl chloroformate (3:6010) from phosgene and trimethylene chlorohydrin (3:8285) (1).]

3:6895 (1) Pierce, Adams, *J. Am. Chem Soc.* 45, 791–792 (1923).

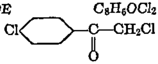
— OCTACHLOROPROPANE C_3Cl_8 Beil. I - 108 I_1-(35) I_2—



B.P. 268—269° at 734 mm. **M.P. 160° (?)**

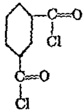
See 3:4450. *Division A: Solids.*

— *p*-CHLOROPHENACYL CHLORIDE $C_8H_6OCl_2$ Beil. VII - 282 VII_1-(152)



B.P. 270° **M.P. 101–102°**

See 3:2990. *Division A: Solids.*

—— ISOPHTHALYL (DI)CHLORIDE  $C_8H_4O_2Cl_2$ Beil. IX - 834
IX₁-(372)

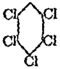
B.P. 276° M.P. 43°

See 3:0520. *Division A: Solids.*

—— 3,4,5-TRICHLOROPHENOL  $C_6H_3OCl_3$ Beil. VI —
VI₁—
VI₂-(181)

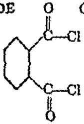
B.P. 271–277° u.c. at 746 mm. M.P. 101°

See 3:2885. *Division A. Solids.*

—— PENTACHLOROBENZENE  C_6HCl_5 Beil. V - 205
V₁-(113)
V₂-(157)

B.P. 275–277° M.P. 86–87°

See 3:2290. *Division A: Solids.*

3:6900 *sym.-o-*PHTHALYL DICHLORIDE  $C_8H_4O_2Cl_2$ Beil. IX - 805
(*sym.-o-*Phthaloyl dichloride) IX₁-(363)

B.P.		M.P.		
276.7°	at 760 mm. (1)	16°	(7)	D_4^{20} = 1.4089 (2)
275.4°	at 726 mm. (2)	15–16° (1)	(8)	1.4060 (6)
269–270°	(3)	13°	(5)	n_D^{20} = 1.5692 (6)
156–157°	at 23 mm. (4)	11.5–12°	(6)	1.56919 (2)
150° cor.	at 23 mm. (5)	11–12°	(7)	$D_4^{15.5}$ = 1.4077 (4)
153.3–153.7°	at 22 mm. (6)			$n_D^{15.5}$ = 1.57099 (4)
131–133°	at 9–10 mm. (7)			

[*See also unsym.-o-phthalyl dichloride* (3:2395).]

The m.p. of ord. samples of C̄ is usually abt. 12°, but distn. at ord. press. (7) yields a prod. with m.p. 16°. The chem. of C̄ is closely connected with that of the isomeric *unsym.-o-*phthalyl dichloride (3:2395) q.v.; for f.p./compn. curve for mixts of the two isomers see (8).

[For prepn. of C̄ from phthalic anhydride (1:0725) with PCl_5 (92% yield (7)) (1) (3) (9) (10), with $PCl_3 + Cl_2$ (12), with benzotrichloride (3:6540) + a little $ZnCl_2$ (13), with a little $ZnCl_2$ at 220° by grad. addn. of $SOCl_2$ (100% yield (14)) (15), or with CCl_4 (etc.) + 2% $ZnCl_2$ at 250–280° (16) see indic. refs.; from phthalic acid (1:0820) with benzotrichloride + a little $ZnCl_2$ see (17).]

[For prepn. of C̄ from *unsym.-o*-phthalyl dichloride (3:2395) by htg. at 150° for 1 hr. see (5); from thiophthalic anhydride [Beil. XVII-486, XVII₁-(256)] with dry Cl_2 at 245° see (18); for formn. as by-product of action of Cl_2 on *o*-toluoyl chloride (3:8740) see (19).]

[For purification of C̄ by treatment with MgO or CaO see (20).]

C̄ on htg. with $AlCl_3$ (½ mole), then decg. cpd. with aq. and extracting with pet. ether, isomerizes (72% yield (7)) (1) (21) to *unsym.-o*-phthalyl dichloride (3,3-dichlorophthalide) (3:2395), m.p. 89°.

[C̄ with Cl_2 at 120–170° in pres. of Fe yields (22) tetrachlorophthalic acid (3:4946).]

[C̄ on reduction with Zn + HCl (23) (24) or HI + P in CS_2 (23) (25) yields phthalide (1:4920); C̄ on boilg. with AcOH + Na/Hg yields (26) phthalyl alcohol (*o*-xylylene glycol) [Beil. VI-910].]

C̄ on heating with K in xylene (27), or with *ter*-bases + $K_2S_2O_5$ (28), or with $ZnCl_2$ + SO_2 at 200° (14) yields phthalic anhydride (1:0725). [Note that last reaction is the reverse of an impt. method (15) of prepn. of C̄.]

[C̄ on shaking for 20 min. at 60° in glass flask with ZnF_2, then extracting with pet. eth. yields (29) *o*-phthalyl difluoride, m.p. 42–43°, b.p. 224–236° at 760 mm. (29); C̄ with HBr gas at 150–160° gives (50% yield (30)) *sym.-o*-phthalyl dibromide, m.p. 78–81° rap. htg., b.p. 191° at 24 mm., 134° at 2 mm. (30).]

[C̄ htd. with a little $ZnCl_2$ and diethyl ether (31) or diethyl phthalate (32) gives (80% yield (31)) ethyl chloride (3:7015).] [Use in mfg. of alkyl chlorides (33).]

[For reactn. of C̄ with glycols see (34); for use of C̄ in acylation of cellulose see (35).]

[For behavior of C̄ with H_2O_2 yielding phthalyl peroxide see (36); with PCl_5 see (37); with NaN_3 see (38) (39); with C_6H_5MgBr see (40).]

C̄ on treatment with cold conc. NH_4OH followed by acidification yields (41) (42) *o*-cyanobenzoic acid [Beil. IX-814, IX₁-(365)], m.p. 190° dec., converted by htg. to phthalimide, m.p. 228.5° u.c. [For reactn of C̄ with dimethylamine yielding *N,N,N',N'*-tetramethyl-*o*-phthaldiamide, m.p. 121–122°, see (43); with diethylamine yielding (44) (45) corresp. *N,N,N',N'*-tetra-ethyl-*o*-phthaldiamide, m.p. 36° (44), 39° (45) see indic. refs.]

C̄ htd. with 1 mole acetamide until no more HCl is evolved gives in good yield (46) *N*-acetylphthalimide, cryst. from toluene, m.p. 135–136° (46); similarly benzamide gives *N*-benzoylphthalimide, m.p. 168° (46).

C̄ reacts instantly with aniline yielding (29) *sym.*-phthalyldianilide, m.p. 253–255°. [Note that when C̄ is treated with aniline in ether or C_6H_6 and stood for some time the prod. has m.p. about 231°; when recrystd. from EtOH, however, the m.p. rises to 253–255°. This apparent anomaly is attributable to the pres. in most samples of C̄ of some phthalic anhydride whose slower reactn. with aniline contaminates the main prod. but is removed by recrystn. from alc. If, on reactn. of ord. C̄ with aniline, the resultant ppt. is filtered at once (before the anhydride has reacted), washed with C_6H_6, alc., and then aq., the prod. shows m.p. 253–255° without recrystn. (29).]

C̄ on hydrolysis yields *o*-phthalic acid (1:0825) q.v.

3:6900 (1) Ott, *Ann.* **392**, 273–277 (1912). (2) Brühl, *Ann.* **235**, 13–14 (1886). (3) Claus, Hoch, *Ber.* **19**, 1187–1194 (1886). (4) von Auwers, Schmidt, *Ber.* **46**, 483 (1913). (5) Garner, Sugden, *J. Chem. Soc.* **1927**, 2878, 2881. (6) Martin, Partington, *J. Chem. Soc.* **1936**, 1181. (7) Ott, *Org. Syntheses*, Coll. Vol. **2** (1st ed.), 528–530 (1943); **11**, 88–91 (1931). (8) Csanyi, *Monatsh.* **40**, 81–92 (1919). (9) Auger, *Ann. chim.* (6) **22**, 295–302 (1891). (10) Tingle, Cram, *Am. Chem. J.* **37**, 603–604 (1907).

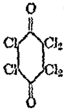
(11) Graebe, *Ann.* **238**, 329 Note (1887). (12) Clemmensen, Miller (to Monsanto Chem. Co.), U.S. 1,974,845, Sept. 25, 1934; *Cent.* **1935**, I 960; *C.A.* **28**, 7265 (1934). (13) Kyrides (to Monsanto Chem. Co.), U.S. 1,963,749, June 19, 1934, *Cent.* **1934**, II 2900; *C.A.* **28**, 5079 (1934). (14) Kyrides, *J. Am Chem. Soc.* **59**, 206–208 (1937). (15) Kyrides (to Monsanto Chem. Co), U.S. 1,951,364, Mar. 20, 1934; *Cent.* **1934**, II 333; *C.A.* **28**, 3424 (1934). (16) Mares (to Monsanto Chem. Co.), U.S 2,051,096, Aug. 18, 1936, *Cent* **1936**, II 3591, *C.A* **30**, 6762 (1936) (17) Kyrides (to Monsanto Chem. Co), U.S. 1,963,748, June 19, 1934; *Cent.* **1934**, II 2900; *C.A.* **28**, 5080 (1934). (18) Ott, Langenohl, Zerweck, *Ber.* **70**, 2360–2362 (1932). (19) Davies, Perkin, *J. Chem. Soc.* **121**, 2213 (1922). (20) Luthy, Thomas (to Monsanto Chem. Works), U.S. 1,906,761, May 2, 1933; *C.A* **27**, 3484 (1933), Brit. 397,775, Sept. 21, 1933; *Cent.* **1933**, II 3194.

(21) Scheiber, *Ber.* **46**, 2366–2370 (1913). (22) Zal'kind, Belikova, Russ. 35,188, Mar. 31, 1934; *Cent.* **1935**, II 1090; *C A.* **30**, 3443 (1936). (23) Hessert, *Ber.* **10**, 1445–1447 (1877). (24) Hessert, *Ber.* **11**, 238–239 (1878). (25) Baeyer, *Ber.* **10**, 123–124 (1877). (26) Hessert, *Ber.* **12**, 646–648 (1879). (27) Pearl, Evans, Dehn, *J. Am. Chem. Soc* **60**, 2479 (1938). (28) Gasopoulos, *Praktika Akad. Athenon.* **6**, 347–353, *Cent.* **1932**, I 3172. (29) Dann, Davies, Hambly, Paul, Semmens, *J. Chem. Soc.* **1933**, 17. (30) Davies, Hambly, Semmens, *J. Chem. Soc.* **1933**, 1309–1315.

(31) Kyrides, *J. Am. Chem. Soc* **55**, 1209–1212 (1933). (32) Kyrides, Dvornikoff, *J. Am. Chem. Soc.* **55**, 4630–4632 (1933). (33) Kyrides (to Monsanto Chem. Co.), U.S. 1,939,216, Dec. 12, 1933; *Cent* **1934**, I 2040, *C.A.* **28**, 1361 (1934). (34) Carothers, Arvin, *J. Am. Chem. Soc.* **51**, 2560–2570 (1929). (35) Brit. 319,584, Nov 20, 1929, *Cent.* **1930**, I 1377. (36) McKee, U.S. 1,614,037, Jan 11, 1927, Brit 271,725, June 23, 1927, *Cent.* **1927**, II 1085, *C.A.* **21**, 745 (1927). (37) Ott, *Ber.* **55**, 2108–2125 (1922). (38) Darapsky, Gaudian, *J. prakt. Chem.* (2) **147**, 47–48 (1936). (39) Lindemann, Schultheis, *Ann.* **464**, 249–253 (1928). (40) Clar, St. John, Hawran, *Ber.* **62**, 940–950 (1929).

(41) Hoogewerff, van Dorp, *Rec. trav chim.* **11**, 91–94 (1892). (42) Scheiber, Knothe, *Ber.* **45**, 2252–2255 (1912). (43) von Braun, Kaiser, *Ber* **55**, 1307–1310 (1922). (44) Maxim, *Compt. rend.* **184**, 690 (1927) (45) French 785,428, Aug. 9, 1935, *Cent.* **1935**, II 3441; *C.A.* **30**, 488 (1936). (46) Evans, Dehn, *J. Am. Chem. Soc.* **51**, 3652 (1929).

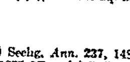
—— **2,3,5,5,6,6-HEXACHLOROCYCLOHEXEN-2-DIONE-1,4** $C_6O_2Cl_6$ **Beil. VII - 574**
VII_1—



B.P. 275–285° dec. **M.P. 89°**

See 3:2360. *Division A: Solids.*

3:6910 2,4,5-TRICHLOROBENZAL (DI)CHLORIDE $C_7H_3Cl_5$ **Beil. V - 303**
(2,4,5-Trichlorobenzylidene (di)chloride) **V_1-(153)**
V_2—



B.P. 280–281° (1) $D_{22}^{22} = 1.607$ **(1)**

Oil which below 0° solidifies to colorless cryst.

[For prepn. of Č from 2,4,5-trichlorotoluene (3:2100) at b.p. with Cl_2 see (1); for formn. of Č from toluene in AcOH/HCl on electrolysis in dark see (6).]

Č on hydrolysis with fumg. H_2SO_4 (2), warm conc. H_2SO_4 (3), or with aq. in s.t. at 260° (4) (1) gives 2,4,5-trichlorobenzaldehyde (3:3375).

[For use of Č in prepn. of dyestuffs see (5).]

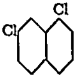
3:6910 (1) Beilstein, Kuhlberg, *Ann.* **150**, 299 (1869). (2) Seelig, *Ann.* **237**, 148–149 (1887). (3) Fischer, Ger. 25,827; June 23, 1883; *Friedländer* **1**, 42 (1877–87) (4) Beilstein, Kuhlberg, *Ann.* **152**, 238–239 (1869) (5) Schmidlin (to Cassella and Co), Ger. 363,290, Nov. 6, 1922; *Cent.* **1923**, II 482; not in *C.A.* (6) Fichter, Glantzstein, *Ber.* **49**, 2484 (1916).

— 2,6-DICHLORONAPHTHALENE $C_{10}H_6Cl_2$ Beil. V - 544 V_1— V_2-(446)

B.P. 285° u.c. M.P. 136°

See 3:4040. *Division A: Solids.*

— 1,7-DICHLORONAPHTHALENE (2,8-Dichloronaphthalene) $C_{10}H_6Cl_2$ Beil. V - 543 V_1-(263) V_2-(446)



B.P. 286° u.c. M.P. 63.5–64.5°

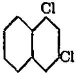
See 3:1385. *Division A: Solids.*

— 1,4-DICHLORONAPHTHALENE $C_{10}H_6Cl_2$ Beil. V - 542 V_1-(262) V_2-(445)

B.P. 286–287° at 740 mm. M.P. 68°

See 3:1655. *Division A: Solids.*

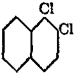
— 1,3-DICHLORONAPHTHALENE $C_{10}H_6Cl_2$ Beil. V - 542 V_1-(262) V_2-(445)



B.P. 291° cor. at 775 mm. M.P. 61–62°

See 3:1310. *Division A: Solids.*

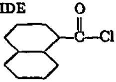
— 1,2-DICHLORONAPHTHALENE $C_{10}H_6Cl_2$ Beil. V - 542 V_1-(262) V_2-(445)



B.P. 295–298° M.P. 34–35°

See 3:0320. *Division A: Solids.*

3:6930 α-NAPHTHOYL CHLORIDE $C_{11}H_7OCl$ Beil. IX - 648 IX_1-(275)



B.P.		M.P.
297.5°	(1)	26° (7)
182–183° at 14 mm.	(2)	22° (5)
172–173° at 15 mm.	(3) (4)	20° (3) (9)
167–168° at 15 mm.	(11)	
158° at 12 mm.	(5)	
168° at 10 mm.	(6)	
163° at 10 mm.	(7) (8)	

[For prepn. of C̄ from α-naphthoic acid (1:0785) with PCl_5 (yield: 100% (4) (8)) (6) (1) (11) in CCl_4 (10) or with $SOCl_2$ (12) (13) (14) (7) see indic. refs.]

C̄ + anhyd. Na_2CO_3 + pyridine treated with a few drops of aq. (14), or C̄ with various RMgX or other organometallic cpds. (15), or C̄ htd. with Ca α-naphthoate (1), gives (80% yield (14)) α-naphthoic acid anhydride, pr. from C_6H_6, m.p. 145–146° (1) (14) (15).

[C̄ on cat. hydrogenation gives (33% yield (5)) α-naphthaldehyde [Beil. VII-400, VII_1-(212)], b.p. 173–174° at 35 mm. (p-nitrophenylhydrazone, m.p. 233–235° (5)).]

[C̄ with $AlCl_3$ + hydrocarbons give corresp. α-naphthyl ketones: e.g., with C_6H_6 (6), biphenyl (8), α-methylnaphthalene (16), β-methylnaphthalene (17) (18), with 2,3- (19), 2,6- and 2,7- (20) dimethyl-naphthalenes, with various subst perylenes (21) (22), see indic. refs.; C̄ with RMgX cpds. also yields corresp. α-naphthyl ketones. e.g., with α-naphthyl MgBr (14) or α-tetralyl MgBr (23), see indic. refs.]

C̄ with aq. hydrolyzes very slowly (9) yielding α-naphthoic acid (1·0785) m.p. 161–162°. — For the amide, anilide, and other derivs. corresp. to C̄ see α-naphthoic acid (1:0785); in addition to these see below

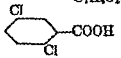
Ⓓ α-Naphthoic β-naphthalide: cryst. from alc., m.p. 200° (13) [From C̄ + β-naphthylamine in C_6H_6 (13).]

3:6930 (1) Hofmann, *Ber.* **1**, 41–42 (1868) (2) Bergmann, Schuchardt, *Ann.* **487**, 253 (1931). (3) Linnell, Roushdi, *Quart. J. Pharm. Pharmacol.* **14**, 270–280 (1941). (4) von Braun, *Ber.* **38**, 180 (1905). (5) Shoesmith, Guthrie, *J. Chem Soc* **1928**, 2332. (6) Reddelien, *Ber.* **46**, 2722, Note 2 (1913). (7) Bell, *J Chem Soc.* **1930**, 1984–1985. (8) Schmidlin, Garcia-Banus, *Ber.* **45**, 3183 (1912). (9) Pope, Winmill, *J. Chem Soc* **101**, 2316 (1912). (10) West, *J Am. Chem. Soc.* **42**, 1662 (1920).

(11) Szperl, Herszaft, *Roczniki Chem.* **14**, 1238–1242 (1934), *Cent.* **1935**, I 2530. (12) Stollé, *J. prakt. Chem.* (2) **74**, 19 (1906). (13) Beckmann, Liesche, Correns, *Ber.* **56**, 354 (1923). (14) Blicke, *J Am Chem Soc* **49**, 2847–2848 (1927). (15) Bruce, *J. Am. Chem. Soc.* **60**, 2277 (1938). (16) Cook, Robinson, *J Chem Soc.* **1938**, 510. (17) Clar, *Ber* **62**, 355–356 (1929) (18) French 614,959, Dec. 27, 1926; *Cent.* **1929**, II 796. (19) Cook, *J. Chem Soc.* **1933**, 1596. (20) Cook, *J. Chem. Soc* **1932**, 492

(21) Zinke, Funke, *Ber.* **58**, 2222–2227 (1925). (22) French 589,643, June 2, 1925; *Cent.* **1926**, I 1053. (23) Fieser, Seligman, *J. Am. Chem. Soc.* **58**, 478–480 (1936).

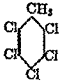
—— **2,5-DICHLOROBENZOIC ACID** $C_7H_4O_2Cl_2$ **Beil. IX - 342**
IX_1-(141)



B.P. 301° **M.P. 155°**

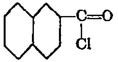
See 3:4340. *Division A: Solids.*

—— **2,3,4,5,6-PENTACHLOROTOLUENE** $C_7H_3Cl_5$ **Beil. V - 303**
V_1-(153)
V_2-(234)



B.P. 301° **M.P. 224-225°**

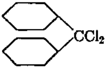
See 3:4937. *Division A: Solids.*

—— β-NAPHTHOYL CHLORIDE  $C_{11}H_7OCl$ Beil. IX-657
IX_1—

B.P. 304–306° **M.P. 51°**

See 3:0900. *Division A: Solids.*

3:6960 α,α-DICHLORODIPHENYLMETHANE $C_{13}H_{10}Cl_2$ Beil. V-590
(Benzophenone (di)chloride; V_1-(278)
α,α-dichloroditan) V_2-(501)



B.P.

305° cor. dec.		(1)	
220°	at 671 mm.	(1)	
235°	at 70 mm.	(2)	
201–202°	at 35 mm.	(3) (4) (15)	
193°	at 30 mm.	(5) (10)	
186°	at 26 mm.	(6)	
189–190°	at 21 mm.	(7)	
172°	at 16 mm.	(8)	
165°	at 12 mm.	(23)	

$D^{18.5}_{18.5} = 1.235$ (1)

Colorless oil showing bluish fluorescence and having only faint odor (3).

[For prepn. of $\bar{C}$ from benzophenone (1:5150) with PCl_5 (yield: 90% (3), 85% (7), 68% (9)) (1) (10) (11) (12) (15); with PCl_5 in C_6H_6 (92% yield (13)), or with oxalyl dichloride (3:5060) in s.t. at 130–140° (14) see indic. refs.; from C_6H_6 + $AlCl_3$ + excess CCl_4 (yield: 90–95% (16), 80–90% (18)) (17) see indic. refs.; for formn. of $\bar{C}$ from diphenylmethane (1:7120) with PCl_5 in s.t. at 170° see (13), from *bis*-(triphenylmethyl) peroxide with PCl_5 (19) or with Cl_2 in CCl_4 in pres. of I_2 (19), from diphenyldiazomethane with $SOCl_2$ or SO_2Cl_2 in pet. ether (100% yield (20)), or from benzotrichloride (3:6540) htd. with uranium metal at 115–128° (4) see indic. refs.]

[For use of $\bar{C}$ in prepn. of acid anhydrides by htg. at 110–120° with salts of aliph. or arom. acids see (21).]

$\bar{C}$ hydrolyzes slowly with cold but rapidly with hot aq. yielding (1) benzophenone (1:5150) and HCl (for study of rate of hydrol. of ether soln. on shaking with aq. see (22)); $\bar{C}$ dis. in conc. H_2SO_4 with yel color (which grad. disappears) and on pouring onto ice yields (6) benzophenone (1:5150); $\bar{C}$ in dry ether shaken 2 hrs. with silver oxide gives (78% yield (23)) benzophenone (1:5150); $\bar{C}$ with alc. NH_3 yields (33) benzophenone.

$\bar{C}$ with MeOH alone (6), with dry MeOH + Mg (24), with dry MeOH in dry pyridine at 0° (25), with NaOMe in MeOH (3) (26), or with NaN_3 in dry MeOH (27) gives (yields: 86% (6) (24), 81% (3)) α,α-dimethoxy-diphenylmethane (benzophenone dimethylacetal) [Beil. VII-415], cryst. from MeOH, m.p. 107–108° (25), 107.5° cor. (24), 106.5–107° (3) (for application to higher alcs. see (3) (26)).

$\bar{C}$ htd. with Ag (11) (5), or stood overnight with Ag or Zn in dry EtOAc (28) cf. (29), or refluxed in CS_2 with 3–4 moles Hg (28) (less Hg gives different result), or with 2 moles NaI in boilg. acetone (30) (1 mole NaI gives different result), or with excess cyclohexyl-MgBr (31) (less reagent gives different result), or with Na in liq. NH_3 (90% yield (32)) or htd. 8 hrs. with diphenylmethane (1:7120) (88% yield (12)) gives tetraphenylethylene [Beil. V-743, V_1-(376)], m.p. 227° cor., 222° u.c. (31), 221° (11). — [$\bar{C}$ does not react with

Mg in dry ether even in pres. of I_2 (28).] — [C̄ refluxed in CS_2 with less than 3 moles Hg (28), or C̄ with 1 mole NaI in acetone in cold (30), or C̄ with 1 mole cyclohexyl MgBr (31), gives tetraphenylethylene dichloride [Beil. V_1-(371)], cryst. from ether, m.p. 186° cor. dec. (31).]

[C̄ with 2 moles Ag azide in ether gives (88% yield (34)) benzophenone diazide, m.p. 42°; C̄ treated as directed (15) with alc. NaSH gives 42–50% yield thiobenzophenone [Beil. VII-429, VII_1-(232)], cryst. from pet. ether, m.p. 53–54° (15) (note that an excess of C̄ must always be present to prevent reduction of the thiobenzophenone to dibenzohydryl disulfide [Beil. VI-681], ndls. from alc., m.p. 152°, and that the latter is obtd. in 70% yield (15) if C̄ is added to the alc. NaSH instead of the reverse); for reactn. of C̄ with diethyl sodio-malonate (2) (9) or with ethyl sodioacetoacetate (8) see indic. refs.; for reaction of C̄ with SbF_3 yielding α,α-difluorodiphenylmethane, b.p. 260° dec., 125° at 10 mm., m.p. −1.8°, $D_4^{20} = 1.1614$, $n_D^{20} = 1.53786$, see (35).]

C̄ with 4 moles aniline in cold gives (36) benzophenone anil [Beil. XII-201, XII_1-(174)] + aniline hydrochloride, the former is sol. in ether, the latter in aq.; sepn. of the layers and addition of alc. to the ether ppts. benzophenone anil, pale yel. lfts. from abs. alc., m.p. 109° u.c. (36) 113°.

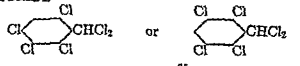
3:6960 (1) Kekulé, Franchimont, *Ber.* **5**, 908–909 (1872). (2) Phalnikar, Nargund, *J. Univ. Bombay* **5**, [illegible] (3) Mackenzie, *J. Chem. Soc.* [illegible] (1935). (5) Anschutz, *Ann.* [illegible] (7) Hsu, Ingold, Wilson, *J.* [illegible] (9) Adickes, *J. prakt. Chem.* (2) **145**, 239 (1936). (10) Gattermann, Schulze, *Ber.* **29**, 2944–2945 (1896).

(11) Behr, *Ber.* **3**, 752 (1870). (12) Norris, Thomas, Brown, *Ber.* **43**, 2958–2959 (1910). (13) Cone, Robinson, *Ber.* **40**, 2161–2162 (1907). (14) Staudinger, *Ber.* **42**, 3976 (1909). (15) [illegible] 574 (1943); **11**, 94–95 (1931). [illegible] (17) Riddell, Noller, *J. Am.* [illegible] –102 (1904); **24**, 1–3 (1905). [illegible]s, Pfenninger, *Ber.* **49**, 1941 (1916).

[illegible] (22) St[illegible] Zechm[illegible] (26) M[illegible] (1909). (28) *Ref.* 12, pp. 2946–2947. (29) Staudinger, Clar, Czako, *Ber.* **44**, 1644 (1911). (30) Finkelstein, *Ber.* **43**, 1532–1533 (1910).

(31) Schmidlin, von Escher, *Ber.* **45**, 894–895 (1912); **43**, 1157, 1159 (1910). (32) Dean, Berchet, *J. Am. Chem. Soc.* **52**, 2825 (1930). (33) Pauly, *Ann.* **187**, 217–220 (1877). (34) Götzky, *Ber.* **64**, 1558 (1931). (35) Henne, Leicester, *J. Am. Chem. Soc.* **60**, 864–865 (1938). (36) *Ref.* 33, pp. 199–202.

3:6980 2,3,4,6-(or 2,3,5,6)-TETRACHLOROBENZAL (DI)CHLORIDE $C_7H_2Cl_6$ Beil. V - 303 V_1-(153) V_2—



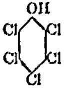
B.P. 305–306° (1) $D^{25}_{-} = $ **1.704** (1)

[For prepn. of C̄ from 2,3,4,6-tetrachlorotoluene (3:2480) or from 2,3,5,6-tetrachlorotoluene (3:2575) at their b.p.'s with Cl_2 (1) or with Cl_2 at 100–130° (especially in light from Hg-vapor lamp) (2) see indic. refs.]

C̄ with strong H_2SO_4 at 90° is hydrolyzed (2) to 2,3,4,6-(or 2,3,5,6-)-tetrachlorobenzaldehyde (3:2700).

3:6980 (1) Beilstein, Kuhlberg, *Ann.* **150**, 303–304 (1869). (2) Cassella and Co., Ger. 290, 209, Feb. 8, 1916; *Cent.* **1916**, I 396–397; not in *C.A.*

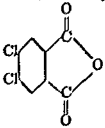
— PENTACHLOROPHENOL C_6HOCl_5 Beil. VI - 194, VI_1-(104), VI_2-(182)



B.P. 309-310° at 754 mm. M.P. 190°

See 3:4850. Division A: Solids.

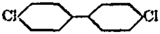
— 4,5-DICHLOROPHTHALIC ANHYDRIDE $C_8H_2O_3Cl_2$ Beil. XVII - 483, $XVII_1$-(254)



B.P. 313° M.P. 187-188°

See 3:4830. Division A: Solids.

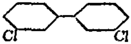
— 4,4′-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ Beil. V - 579, V_1-(273), V_2-(484)



B.P. 315° M.P. 148°

See 3:4200. Division A: Solids.

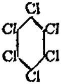
— 3,3′-DICHLOROBIPHENYL $C_{12}H_8Cl_2$ Beil. V - 579, V_1-(272), V_2-(484)



B.P. 320° M.P. 29°

See 3:0180. Division A: Solids.

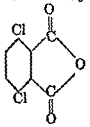
— HEXACHLOROBENZENE C_6Cl_6 Beil. V - 205, V_1-(113), V_2-(157)



B.P. 326° M.P. 229°

3:4939. *Division A: Solids.*

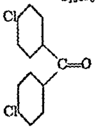
—— 3,6-DICHLOROPHTHALIC ANHYDRIDE $C_8H_2O_3Cl_2$ Beil. XVII - 483
XVII$_1$-(254)



B.P. 339° M.P. 194°

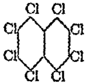
See 3 4860. *Division A: Solids.*

—— 4,4'-DICHLOROBENZOPHENONE $C_{13}H_8OCl_2$ Beil. VII - 420
VII$_1$-(228)



B.P. 353° at 757 mm. M.P. 145°

See 3:4270. *Division A: Solids.*

—— OCTACHLORONAPHTHALENE  $C_{10}Cl_8$ Beil. V - 547
V$_1$—
V$_2$-(446)

B.P. 440–442° M.P. 203°

See 3.4893. *Division A: Solids.*

CHAPTER XVI

DIVISION B. LIQUIDS WITH BOILING POINTS REPORTED AT ORDINARY PRESSURE

Section 2. D_4^{20} less than 1.1500

(3:7000–3:7499)

3:7000 CHLOROACETYLENE HC≡C—Cl C_2HCl Beil. I - 244
(Chloroethyne) I_1-(106)
I_2-(221)

B.P. −29.6° (1)
−32 to −30° (2)

[*See also dichloroacetylene* (3:5010).]

C̄ is a gas with extremely nauseating odor reminiscent both of yellow phosphorus and of carbylamines; its inhalation even in traces produces very unpleasant symptoms. It is also treacherously explosive and may detonate during manipulation (2).—C̄ ignites spontaneously in air (6) (3).

[For prepn. of C̄ from *cis*-1,2-dichloroethylene (3:5042) via treatment in dil. alc. with aq. alk. $Hg(CN)_2$ to yield $Hg(C{\equiv}CCl)_2$ (see below) which is then warmed (under N_2) with alk. NaCN soln. see (1) (2) (3) (4)] cf. (7).

[For formn. of C̄ during reaction of 1,1,2,2-tetrachloroethane (acetylene tetrachloride) (3:5750) with solid KOH see (5); from 1,2-dichloroethylene with alc. KOH see (3) (4); from β,β-dichloroacrylic acid (3:1875) with $Ba(OH)_2$ see (6).]

C̄ with $NH_4OH/CuCl$ gives (3) (6) an explosive ppt.—C̄ with $NH_4OH/AgNO_3$ gives (2) (3) a ppt. of silver salt, which is extremely explosive, detonating with great violence not only in dry state but also when moist *and even under water*, quantities as small as 0.1 g. causing considerable damage (2).

C̄ with aq. alk. $Hg(CN)_2$ yields (3) (4) (1) (2) a mercury salt, $Hg(C{\equiv}CCl)_2$, cryst. from $CHCl_3$ (1) (2) (3) (4), m.p. 185° (1) (4), 186° (2); explodes at 195° with flame and deposition of soot (3) (4). [This prod. with alk. KCN evolves C̄ (use in prepn. of C̄ as above).]

C̄ with Br_2/aq. yields (6) 1-chloro-1,1,2,2-tetrabromoethane [Beil. I-95], m.p. 33–34° (6).

[For other reactns. see (2) (7); for study of oxidation of C̄ see (1).]

3:7000 (1) Bashford, Emeléus, Briscoe, *J. Chem. Soc.* **1938**, 1358–1364. (2) Ingold, *J. Chem. Soc.* **125**, 1535–1536 (1924). (3) Hofmann, Kirmreuther, *Ber.* **42**, 4232–4238 (1909). (4) Hofmann, Kirmreuther, *Ber.* **41**, 314–317 (1908). (5) Sastry, *J. Soc. Chem. Ind.* **35**, 450–452 (1916). (6) Wallach, *Ann.* **203**, 87–94 (1880). (7) Ott, Dittus, Weissenburger, *Ber.* **76**, 87–88 (1943).

3:7005 CHLOROMETHANE CH_3Cl CH_3Cl Beil. I - 59
(Methyl chloride) I_1-(8)
I_2-(11)

B.P.	M.P.	
−24.22° at 760 mm. (1)	−97.72° (1)	$n_D^{-42.5} = 1.3830$ (5)
−23.7° at 760 mm. (3) (4)	−96.65° (2)	

Colorless gas with ethereal faintly sweet non-irritating odor. — Important comml. fluid for refrigerating systems; for extensive reviews of properties, uses, handling, toxicity, hazards, etc., see (4) (5) (6). — For b.p. at various pressures from 26–761 mm. together with extensive thermodynamic data see (1) (4). — Solubility of C̄ (in cc.) in 100 cc. solvent at 20°C and 760 mm.: water, 303; EtOH, 3740; AcOH, 3679; CCl_4, 3756; C_6H_6, 4723 (4); for extensive data on solubility of C̄ in other solvents see (7) (8) (9).

[For prepn. of C̄ from MeOH (1:6120) with conc. H_2SO_4 + NaCl (10); with conc. HCl + $ZnCl_2$ (yield: 79% (11), (12)); with HCl gas + various catalysts (13) (14) (15); with PCl_3 + $ZnCl_2$ (68% yield (11)); with PCl_5 + $ZnCl_2$ (72% yield (11)); with $SOCl_2$ + pyridine (80% yield (11)); with $AlCl_3$ (100% yield (16)); with $FeCl_3$ (17) (20) see indic. refs.; for prepn. of C̄ from Me_2SO_4 with strong HCl (or NaCl) (90% yield (18)) or with $AlCl_3$ (100% yield (19)) see indic. refs.] [For study of mechanism of formn. of C̄ from MeOH + HCl see (24).] [For formn. (53% yield) from NH_4Cl with diazomethane in ether see (36).]

[For study of drying of C̄ see (21); for detn. of aq. in C̄ see (22); for study of pyrolysis see (23); for behavior with Na see (25).]

C̄ on warming with NaI in MeOH or EtOH gives (26) methyl iodide, b.p. 42°. [Use in detection and detn. of C̄ (26).]

C̄ is inflammable in air within range 8.1–17.2% by vol. (4) (28) cf. (35). — [For study of detn. of C̄ via combustion see (27) (29) (31) (32).] — C̄ on burning in presence of copper gives strong Beilstein test; [use in detection and detn. of C̄ in air and foods (29); for testing device see (30)].

[For detn. of C̄ by absorption in AcOH see (27); for detn. of small amts. of C̄ in air (31) (37) or in mixts. with other gases (32) see indic. refs.]

Ⓓ *Acetanilide: m.p. 112–113° u.c. (33). [From C̄ via conversion to CH_3MgCl and* reaction with phenyl isocyanate (33); note that C̄ with Mg in dry ether + trace I_2 gives in 4 hrs. (99.7% yield) MeMgCl (38).]

—— *N*-Methyl-3-nitrophthalimide: ndls. from CS_2, m.p. 112–113° (34). [Not recorded directly from C̄ but from MeI by reactn. with K 3-nitrophthalimide, probably therefore from C̄ + NaI + K 3-nitrophthalimide in MeOH.]

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3:7010 CHLOROETHENE $CH_2{=}CHCl$ C_2H_3Cl Beil. I - 186
(Vinyl chloride) I_1-(77)
I_2-(157)

B.P. −13.9° at 760 mm. (1) **F.P. −159.7° (1)**

Colorless gas easily liquefied by cooling. — For b.p.'s at various pressures from 39.5–760.3 mm. see (1). — Readily polymerizes in light or in dark if catalysts are present. The literature on polymerization of $\bar{C}$ and on its polymers and copolymers is extremely extensive and cannot be treated here.

[For prepn. of $\bar{C}$ from 1,2-dichloroethane (ethylene dichloride) (3:5130) by action of alc. KOH (85% yield (2)) see (2) (3); for prepn. of $\bar{C}$ from acetylene by addn. of HCl see (4) (5) (14) (15) + Beil.; for purification of $\bar{C}$ with conc. H_2SO_4 see (8).]

$\bar{C}$ as liq. + SO_2 as liq. in 95% alc. + catalyst gives ppt. (6) of insol. pdr. of vinyl chloride polysulfone $[(CH_2{=}CHCl)_2.SO_2]_n$, darkens 135–140°, melts 250–275° (6); on hydrolysis with 20% aq. NaOH this polymer gives (7) acetaldehyde (1:0100) q.v.

$\bar{C}$ adds HBr to give according to conditions (9) (10) either 100% 1-chloro-1-bromoethane (ethylidene chlorobromide), b.p. 82.7° at 760 mm. (11), b.p. 80.5–81.5° at 735 mm. (9), $n_D^{20} = 1.4660$ (9), or 1-chloro-2-bromoethane (ethylene chlorobromide), b.p. 106.7° at 760 mm. (12), b.p. 104–105° at 735 mm. (9), $n_D^{20} = 1.4908$ (9). [Note: the ethylidene chlorobromide may be further identified by htg. with moist silver oxide in a s.t. for 5 hrs. at 100° giving acetaldehyde (1:0100) q.v.; the ethylene chlorobromide may be further identified by refluxing with aniline to yield N,N'-diphenylethylenediamine, m.p. 63.5–64° (9).]

$\bar{C}$ with HI yields only (9) 1-chloro-1-iodoethane (ethylidene chloroiodide), b.p. 117–119° (13), 114–115° (9).

$\bar{C}$ adds Br_2 yielding (16) (17) 1-chloro-1,2-dibromoethane, b.p. 159–160° (16); 163° at 760 mm., 48° at 12 mm.; $D_4^{19} = 2.248$; $n_D^{19} = 1.554$ (17); for study of this photochem. reaction see (18).

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3:7015 ETHYL CHLORIDE CH_3CH_2Cl C_2H_5Cl Beil. I - 82
(Chloroethane) I_1-(23)
I_2-(50)

B.P.		F.P.	
+13.1° at 760 mm. (1) (2)		−142.5° (15)	[D_4^{15} = 0.90280 (11)]
12.6° (3)		−141.6° (16)	n_D^0 = 1.3790 (10)
[12.5–12.6° at 725 mm. (4)]		−140° (17)	D_{12}^{12} = 0.8510 (19)
12.52° (5)		−139.4° (18)	n_D^{-20} = 1.3913 (2)
12.50° (6)		−138.7° (1)	D_8^8 = 0.9176 (12)
12.5° (7) (8) (9)		−136.4° (11)	n_D^{-30} = 1.4085 (2)
12.4° (10)			D_0^0 = 0.92138 (20)
12.3° at 760 mm. (11)			
12.18° at 760 mm. (12)			
12–12.5° (13) (14)			

Colorless mobile liq. with pungent ethereal odor and sweetish taste. — C̃ is inflammable (see also below) and burns with smoky green-edged flame producing fumes of HCl.

SELECTED PHYSICAL PROPERTIES

Vapor pressure. [For vapor-press. data over various temp. ranges, e.g., from −30 to +40° (5), −30° to 100° (21), 12–187° (4) (22), see indic. refs.]

Solubility relations. C̃ is very spar. sol. aq., e.g., 100 g. aq. at 0° dis. 0.447 g. C̃ (23), 0.570 wt. % (24), although even this is somewhat more than its homologs (24).

C̃ is miscible with EtOH although forced out of soln. by addn. of aq. (25); for use of mixt. of EtOH (50–80%) + aq. (50–20%) as selective solv. for C̃ in sepn. from butane see (26). — C̃ is also miscible with ether. — [For study of rate of volatilization of C̃ from solns. in ether or oils see (32).]

[For soly. of C̃ in CCl_4 (3:5100) or in ethylene dichloride (3:5130) at −10° and 20° and at 100–760 mm. press. see (27); for soly. of C̃ in various high-boilg. ethers and esters of interest to refrigeration industry see (28) (29); for solubility, density, b.p., vapor/liq. equil., etc., of system C̃ + kerosene see (30); for sepn. of C̃ from butane by azeotropic distn. with SO_2 see (31).]

[For soly. in C̃ of anhydrous $FeCl_3$ (33) (34) or anhydrous $AlCl_3$ (35) (36) see indic. refs.]

Adsorption of C̃. [For studies on adsorption of vapors of C̃ by activated carbon at −15° (37), 0° (37) (38), 20° (37), 25° (39), or 50° (40) see indic. refs. and also (41); for sepn. of C̃ from ethylene + HCl gas by adsorption on carbon see (42). — For adsorption of vapors of C̃ by dehydrated chabasite see (43).]

Inflammability of C̃ or its mixtures. C̃ is readily inflammable; in mixts. with air explosive range conts. 4.00–14.18 vol. % C̃ with minimum ignition temp. 517°C. (44) cf. (47) (48); in mixts. with O_2 explosive range conts. 4.05–67.2 vol. % C̃ (44) (45) with min. ignition temp. 468°C; in mixts. with N_2O explosive range conts. 2.1–32.8 vol. % C̃ (45) cf. (46); for study of explosion range of C̃ + $C_2Cl_2F_2$ ("Freon") + air or C̃ + butane + air see (49). — See also below under use of C̃ as anesthetic.

Other miscellaneous physical props. [For study of thermal conductivity of C̃ see (50).]

Binary systems contg. C̃. [For f.p./compn. data and diagram of system C̃ + methylene (di)chloride (3:5020), eutectic, f.p. −149.7°, contg. 68.3 wt. % C̃, see (18); for f.p./compn. data and diag. of system C̃ + EtBr (note no eutectic is formed) see (18); for system C̃ + solid CO_2 see (8).]

TOXICITY AND PHYSIOLOGICAL ACTION OF C̄

Full treatment of this topic is beyond the scope of this work; however, for lead references on its pharmacology (51), toxicity (52) (53) (54) (55), or anthelmintic props. (56) see indic. refs. — For use as narcotic and anesthetic see below.

USES OF C̄

Use for anesthesia and narcosis. [For general reviews on use of C̄ as anesthetic see (57) (58) (59) (60); for use of C̄ as dental anesthetic see (61) (62) (63); for short narcosis see (64) (65). — For data on mortality from use of C̄ as anesthetic see (66). — For studies of explosion hazards with C̄ or C̄ + ether (67) especially in presence of X-ray apparatus (68) see indic. refs. (see also above under inflammability of C̄).]

Use as a refrigerant. C̄ either alone or mixed with other cpds. is often used in refrigerating systems: e.g., for general survey of this aspect see (21); for examples of patents on use in refrigerating systems of C̄ (70), of C̄ (96%) + MeCl (4%) (3:7005) (71), of C̄ (25%) + methylene (di)chloride (3:5020) (75%) (72), of C̄ (40%) + EtBr (60%) (72), of C̄ + an alc. + a hydrocarbon lubricant (74) see indic. refs. — For study of use of C̄ with other suitable liq. in low-temp. cryostats see (18).

Use as solvent for extraction of oils. For use of C̄ as extremely volatile solvent for extraction of oils, fats, resins, perfumes, etc., see (75) (76) (77).

Miscellaneous uses of C̄. C̄ is now an important raw material in the prepn. of tetraethyllead for use as an anti-knock agent in gasoline; for further details see below under chem. behavior of C̄ toward metals.

[For use of C̄ in purification of metallic mercury see (78).]

Because of its inertness toward ozone, its availability, and its low b.p., C̄ is often used as solvent for ozonolysis.

DETERMINATION OF C̄

For detn. of C̄ by pyrolytic dissociation at 900° into ethylene and HCl, followed by detn. of chloride ion with stand. $AgNO_3$ (42) (80) cf. (81) or by combustion with O_2 in an explosion pipet to yield H_2O, CO_2 + HCl (47), see indic. refs. — For detn. of C̄ by hydrolysis with excess std. $N/2$ alc. KOH in s.t. at 120° for 15 min. and back titration with $N/2$ HCl see (79).

For detn. of C̄ in $CHCl_3$ (3:5050) see (82); for detection of C̄ in perfumes see (83).

For further aspects of identification of C̄ see below under Ⓓ.

PREPARATION OF C̄

C̄ can be *prepared from various sources and by many methods (see amplification below)*; however, for quick laboratory methods the most convenient are those from EtOH by htg. with $AlCl_3$ (1 mole) at 150° (97.6% yield (13)) and from diethyl sulfate with aq. $CaCl_2$ (63% yield (84)).

From ethyl alcohol (1:6130).

With hydrogen chloride or hydrochloric acid. [For prepn. of C̄ from EtOH by reactn. with HCl in absence of cat. under reflux (85) (86) or at 125° and 16 atm. (87), or 140° and 24 atm. (88), *see indic. refs.; for use of EtOH + liq. HCl see (89).]*

For prepn. of C̄ from EtOH with conc. HCl in pres. of $ZnCl_2$ (60% yield (7) (91)) see articles represented by (90) (7) (91) (92) (93) [for patents (often including also other metal salt cat. such as $BiCl_3$, etc.) see (94)–(102), incl.].

[For prepn. of C̄ from EtOH + HCl in pres. of H_3PO_4 (103) (104) (105) or H_2SO_4 (106) or $EtHSO_4$ (107) see indic. refs.]

By use of metal salts For prepn. of $\bar{C}$ from EtOH by use of $AlCl_3$ at 150° (97.6% yield (13)) or of aq $FeCl_3$ at 80° (108), or by reflux with subl. $FeCl_3$ for 1½ hrs. (86% yield (112)), see indic. refs.

By use of inorganic acid chlorides. For prepn. of $\bar{C}$ from EtOH by use of PCl_3 (43% yield (109)), $PCl_3 + ZnCl_2$ (62% yield (91)), $PCl_5 + ZnCl_2$ (70% yield (91)), $SOCl_2$ + pyridine (75% yield (91)), or SO_2Cl_2 + pyridine (110) see indic. refs.

By use of organic acid chlorides. {For prepn. of $\bar{C}$ from EtOH with benzotrichloride (3:6540) + $FeCl_3$ see (111)}

From diethyl ether (1:6110).

By cleavage with HCl + a catalyst. {For prepn of $\bar{C}$ from diethyl ether with HCl + $ZnCl_2$ (113) at 80–280° under press. (114) or at 300–370° under press. (115), or with HCl + $AlCl_3/NaCl/FeCl_3$ at 200–325° (116), or with HCl + a nitrogen heterocycle (117) see indic. refs}

By cleavage with acid chlorides + a catalyst. {For prepn of $\bar{C}$ from diethyl ether with $SOCl_2$ or S_2Cl_2 in pres. of $SnCl_4$ or $TiCl_4$ (118), or with $SOCl_2 + ZnCl_2$ (119); or with benzoyl chloride (3:6240) in pres of Zn (120) cf. (121), $ZnCl_2$ at 150° (78% yield (122)) cf. (123) (124), MeZnI (125) or $AlCl_3$ (126), or with phthalyl (di)chloride (3:6900) in pres. of $ZnCl_2$ at 170° (80% yield (122)); or with acetyl chloride (3:7065) in pres. of $ZnCl_2$ (127) or $AlCl_3$ (126) see indic refs.}

{For formn. of $\bar{C}$ from diethyl ether + $CHCl_3$ (3:5050) + cat. at 290° and 25 atm. see (128)}

From various ethyl esters of inorganic and organic acids. {For prepn. of $\bar{C}$ from diethyl sulfate with aq $CaCl_2$ as lab method (63% yield (84)) or as manufacturing process (129); from diethyl sulfate with conc HCl at 140° and 24 atm. (130), from ethyl chlorosulfonate with fumg. HCl at 100° (91% yield (131)) (132) cf. (189), pyridine (133), or di-*n*-butylamine at 100° (53% yield (134)) see indic. refs.}

{For prepn. of $\bar{C}$ from ethyl formate (1:3000) with $AlCl_3$ (1 mole) at 110° (82% yield (135)); from ethyl chloroformate (3:7295) on htg. at 250° (for study of this reaction see (136) (137)), with dimethylaniline at 150° (138), with pyridine (139), with quinoline at 100° (139) or even 59° (140) (141), or with $AlCl_3$ at room temp (142), or with $EtHSO_4$ (143) see indic. refs.}

{For prepn. of $\bar{C}$ from ethyl acetate (1:3015) with subl. $FeCl_3$ on 1½ hrs. reflux (73% yield (112)), or with $SiCl_4$ (144), from ethyl benzoate (1:3721) with subl. $FeCl_3$ on 1½ hrs. reflux (74% yield (112)); or from diethyl phthalate (1:4331) with phthalyl (di)chloride (3:6900) + trace $ZnCl_2$ at 130° (145) see indic. refs.}

From vinyl chloride (3:7010). {For prepn. of $\bar{C}$ from vinyl chloride by cat. hydrogenation at elev. temp. and press see (146)}

From ethane. {*For prepn. of $\bar{C}$ from ethane with Cl_2 above 290° in pres. of ethylene or* $PbEt_4$ as cat. (yields 67.8–71.4% (147)) (148) see indic. refs. — For examples of other patents on prepn. of $\bar{C}$ from ethane with Cl_2 in pres. of various cat. (149) (150) (151) (152) (153) see indic refs.}

From ethylene. The preparation of $\bar{C}$ from ethylene by catalytic addn. of hydrogen chloride has been extensively studied both in the scientific and in technical literature. At very low temperatures, the catalyzed reaction is quantitative, but as the temperature is increased the reverse reaction (dissociation of $\bar{C}$ into ethylene and HCl) is favored.

{For studies on the prepn. of $\bar{C}$ from ethylene with HCl in pres. of $AlCl_3$ or $BiCl_3$ at −78° (100% yield (3) (153)), or as high as −12° (95% yield (154) (155)) or 130° (37% yield (42)), see indic refs.; for studies on equilibrium at 114° and 124° (156), at 170°, 200°, and 230° (157) or for calcn. of entropy of system (158) see indic. refs.; for study of various cat. see (159)}

[The patent literature on prepn. of C̄ from ethylene + HCl is extensive and overlapping, but illustrative examples may be cited. For patents involving use of $AlCl_3$ (160) (161) under pressure (162) (163) (164) (165) in the pres. of a solvent (often C̄ itself) (162) (166) (167) (168) (190) see indic. refs. — For use of ethylene + mixt. of HCl (90%) + Cl_2 (10%) + $AlCl_3$ (169) (170) or for prepn. (171) or revivification (172) of $AlCl_3$ cat. see indic. refs.]

[For patents on prepn. of C̄ from C_2H_4 + HCl with various cat., e.g., with $BiCl_3$ (173) (174) (175), with anhydrous $EtHSO_4$ (176), with $SnCl_4$ on activated carbon at 150° (177), with bauxite cat. (178), with iron oxide cat. at 50° and ord. or increased press. (179), with $BaCl_2$ at 250° (180), with $FeCl_3$ in C̄ or $AlCl_3$ in nitrobenzene (181), with $ZnCl_2$ on activated carbon, silica gel, etc., (182) (183), with various surface agts. (184) (185), with SO_2 (186), with 90% H_2SO_4 + NaCl (188), or in liq. ethyl chlorosulfonate + $BiCl_3$ (189) see indic. refs.]

[For purification of C̄ obtd. from techn. gases by HCl method see (187).]

From miscellaneous sources. [For formn. of C̄ from EtBr with $CHCl_3$ (3:5050) in pres. of $AlCl_3$ at 50° (191), from EtMgBr during reaction with S_2Cl_2 (192) or with 1,2-dichloroethylene (3:5030) (193), from EtI with Hg_2Cl_2 in s.t. at 140° (12), from ethyl α,β-dichlorovinyl ether (3:5540) with Cl_2 at ord. temp. followed by warmg. or stdg. in absence of aq. (194), or from dichloroacetaldehyde diethylacetal (3:6110) with $ZnEt_2$ (195) see indic. refs.]

[For formn. of C̄ from succinic acid (1:0530) with aq. $FeCl_3$ in sunlight (196) or from MeCl (3:7005) + aq. by disproportionation over cat. at 200–275° (197) see indic. refs.]

CHEMICAL BEHAVIOR OF C̄

Pyrolysis of C̄

C̄ passed through plain tube at 410° is largely unchanged, but C̄ passed at 550° through tube contg. pumice (198) cf. (42) or other cat. (199) dissociates completely into ethylene + HCl (use in detn. of C̄ (42)).

Behavior of C̄ with Inorganic Reactants

Chlorination. [C̄ with liq. Cl_2 (1 mole) in u.v. light and cooling yields (200) mainly 1,1-dichloroethane (3:5035) accompanied by some 1,2-dichloroethane (3:5130) and higher chlorination prods.; the two dichloroethanes are also obtd. from C̄ with Cl_2 + aq. (201). — For very impt. study of behavior of C̄ with Cl_2 at 202–380° see (202) (147).]

[C̄ with $SbCl_5$ in s.t. at 100° (203) or C̄ with NCl_3 (204) yields 1,2-dichloroethane (ethylene dichloride) (3:5130).]

Bromination. [For behavior of C̄ with Br_2 see (207) (208).]

Fluorination. [C̄ at 900° with F_2 in pres. of Cu yields (205) CF_4, CF_3Cl, $CF_3.CF_2Cl$, $CHF_2.CH_2Cl$, $CF_2{=}CCl_2$, and other prods.]

Hydrogenation. [For behavior of C̄ with atomic hydrogen see (206).]

Hydrolysis. [C̄ over suitable partially dehydrated $Al(OH)_3$ at room temp. (209), or C̄ + aq. vapor over cat. at 300–500° at ord. press. (210) (211) (212), or C̄ with aq. NaOH above 150° under press. (213), or C̄ with alc. NaOH (214), alc. Na_2CO_3, MgO, or CaO (215) is saponified yielding EtOH (1:6130). — The reaction of C̄ with EtOH/KOH is bimolecular (216); furthermore during hydrol. of C̄ with alk. some diethyl ether is always formed cf. (213) (214) and the reaction may be adapted to its prepn. (217).]

Amination. [C̄ with alc. NH_3 in s.t. at 100° (218) or C̄ with liq. NH_3 at 220° and 220 atm. press. (219) gives salts of ethylamine, diethylamine, triethylamine, and other prods. —

C̄ with $NaNH_2$ in liq. NH_3 at 0° and 20 atm. gives ethylamine (30% *yield* (220)) and ethylene.]

Behavior of C̄ with inorganic acids. [C̄ passed through boilg. H_2SO_4 gives C_2H_4 + SO_2 + HCl; C̄ is absorbed by SO_3 giving a liq. which probably comprises a mixture of ethyl chlorosulfonate, β-chloroethanesulfonic acid, and β-hydroxyethanesulfonyl chloride (221).]

Behavior of C̄ with inorganic salts. [For study of rate of reaction of C̄ with KI in acetone at 50° and 60° see (222). — C̄ with $AlBr_3$ under suitable cond. yields (223) ethyl bromide.]

Behavior of C̄ with metals. *With sodium.* The most important reaction of C̄ with metals is that involved in the manufacture of tetraethyllead for use as an anti-knock agent in motor fuels. Tetraethyllead is prepared for C̄ either by direct reaction with Na/Pb alloys, or by reaction with Mg and subsequent conversion of the EtMgCl by means of $PbCl_2$. For a general survey (without references) on the manufacture of tetraethyllead see (224).

For patents involving the prepn. of Et_4Pb from C̄ by reactn with Na/Pb alloys under various circumstances see (225)–(244) incl.; for patents involving the use of EtMgCl see (245)–(248) incl.

[For behavior of C̄ with Na in lgr. followed by CO_2 (249) or with amyl-sodium or octyl-sodium (250) *see indic. refs.* — C̄ with K/Na alloy in xylene gives (251) ethane (32%) and ethylene (5.5%). — C̄ with Tl/Na yields (252) $TlEt_3$.]

With magnesium. [C̄ with Mg in s.t at 260° for 4 hrs gives (253) gas (consisting of 45% butane + 20% olefins + 22% H_2) and a white solid which with aq. gives a gas contg. 86% H_2 + 13% ethane]

C̄ with Mg in dry ether in absence of air and in pres. of trace of I_2 gives (99.7% yield in 4 hrs. (254)) EtMgCl; this reagt. is actually an equil. mixt. contg. 25% EtMgCl + 42.5% $MgEt_2$ + 42.5% $MgCl_2$ (255). — For study of competitive reaction with Mg in ether of an equimolar mixt of C̄ + EtI yielding 27% EtMgCl + 73% EtMgI see (256). — [For reactn. of EtMgCl with NH_4Cl or triethylamine.HCl (254), with NH_2Cl (257), or with NCl_3 (258) see indic. refs.; for study of electrolysis of EtMgCl in ether see (259). — For reactn of EtMgCl with $PbCl_2$ yielding $PbEt_4$ see (245)–(248) incl ; with C_6H_5NCO *yielding propionanilide see below under* Ⓓ's.]

Behavior of C̄ with Organic Reagents

[C̄ with C_6H_6 + Al/Hg gives (76% *yield* (260)) ethylbenzene (1:7410); C̄ + hexane + $AlCl_3$ gives (261) octane.]

[C̄ with CO + $AlCl_3$ at 40–50° and 120 atm. followed by treatment with H_2O gives (43% yield (262)) (263) propionic acid (1:1025).]

[C̄ with ethylene oxide (1:6105) + $AlCl_3$ gives (264) a mixt. contg. 4-chlorobutanol-1 (3:9170) + ethylene chlorohydrin (3:5552).]

[C̄ may be used for the ethylation of OH groups or NH_2 groups: e.g., for reaction of C̄ with sodium phenolate yielding (265) ethyl phenyl ether (1:7485) or for use of C̄ in ethylation of cellulose (266) (267) see indic. refs.; for use of C̄ in ethylation of metanilic acid (268) (214) (215), *o*-toluidine (269), or *m*-aminophenol (268) see indic. refs.]

[For condens. of C̄ with *hexamethylenetetramine see* (270).]

[C̄ (2 moles) with ethylene (di)bromide (1 mole) + 3% $AlCl_3$ in steel bomb at 25° for 14 days undergoes a redistribution reactn. yielding (271) a mixt. consisting of 5 cpds., viz., C̄ (35 mole %) + EtBr (30 mole %) + ethylene chlorobromide (17 mole %) + ethylene (di)bromide (11 mole %) + ethylene dichloride (3.5130) (7 mole %).]

[C̄ (1 mole) with quinoline (1 mole) in s.t. in direct sunlight reacts only very slowly (incomplete in 1 year) but grad. separates ethylquinolium chloride, cryst. from abs. EtOH by addn. of dry ether, m.p. 122° (290).]

Ⓓ Propionanilide: m.p. 104.0–104.5° u.c. (272). (See also under propionic acid (1:1025).) [From C̄ by conversion to EtMgCl (see above) and reactn. in dry ether with phenyl isocyanate (272).]

—— Propion-*p*-toluidide: m.p. 123°. [Presumably obtainable (272) from C̄ via conversion to EtMgCl (see above) and reaction in dry ether with *p*-tolyl isocyanate.]

—— Propion-α-naphthalide: m.p. 126° u.c. (273). [Presumably obtainable (272) from C̄ via conversion to EtMgCl (see above) and reaction in dry ether with α-naphthyl isocyanate; the analogous process for EtBr has been reported (273).]

—— Ethyl mercuric chloride: m.p. 193.5° cor. (274), 192.5° (275), 192° (276). [Prepd. indirectly (276); but should be preparable from EtMgCl with $HgCl_2$ since corresp. EtHgBr has been reported (276) from EtMgBr + $HgBr_2$. — Note that m.p. of EtHgCl is almost identical with that (193.5°) of EtHgBr cf. (276).]

—— *S*-(Ethyl)isothiourea picrate: m.p. 188° (277). [Not reported from C̄, but readily obtd. from EtBr or EtI (277) (278) (1 g.) with thiourea (1 g.) in alc. (10 ml.) on refluxing for 2 hrs., then adding PkOH (1 g.), htg. until clear soln. results, then cooling (277). — Note that the m.p. of this prod. is very close to those of *S*-(*sec*-butyl)isothiourea picrate, m.p. 190° (278), and *S*-benzylisothiourea picrate, m.p. 188° (277).]

—— *N*-Ethylphthalimide: [Beil. XXI-461, XXI_1-(363)], ndls. from alc., m.p. 79° (279), 78° (280). [Prepd. indirectly (280), also from EtI with potassium phthalimide in s.t. at 150° (279).]

—— *N*-Ethyl-3-nitrophthalimide: pl. from CS_2, m.p. 105–106° (281) (282); for photographs of crystals see (282). [Not reported from C̄ itself, but obtd. from EtBr with K phthalimide on protracted reflux. (281).]

—— *N*-Ethyltetrachlorophthalimide: pl. from $CHCl_3$ on pouring into 2 vols. EtOH, m.p. 192–193° (283). [Not reported from C̄ but obtd. from EtBr or EtI with K *tetra*-chlorophthalimide in s.t. at 200° for 6 hrs. (283).]

—— *N*-Ethylsaccharin: cryst. from dil. alc., m.p. 94° (284). [This prod. cannot be obtd. from C̄ itself (284) but is obtd. from either EtBr or EtI with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 30 min. (284).]

—— *N*-Ethyl-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide: m.p. 113 5° u c. (285). [Not reported from C̄ but obtained from EtBr with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide (285).]

—— *p*-Ethoxybenzoic acid: m.p. 195° (286) cf. (287).

—— Ethyl 2,4,6-triiodophenyl ether: m.p. 83.5° cor. (288).

—— Ethyl α-naphthyl ether: oil, b.p. 280.5° cor., f.p. below −10° (289). (Corresp. picrate, m.p. 118.5–119.5° cor.; Neut. Eq. 401 (289).)

—— Ethyl β-naphthyl ether: m.p. 35.5–36 0° cor., b.p. 282° cor. (289). (Corresp. picrate, m.p. 101.0–101.5° cor., Neut. Eq. 401 (289).)

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3:7020 2-CHLOROPROPENE-1 (Isopropenyl chloride α-methylvinyl chloride) $CH_3-C(Cl){=}CH_2$ C_3H_5Cl **Beil. I - 198** I_1-(82) I_2-(169)

B.P.		F.P.		
22.65°	at 760 mm. (1)	**−138.6°** (2)	D_4^0 = **0.918** (5)	n_D^{20} = **1.3949** (4)
22.6°	at 760 mm. (2)	**−137.4°** (1)		
22.5–23.5°	at 760 mm. (3)			
21.7–21.8°	at 743 mm. (4)			

[For prepn of $\bar{C}$ (45%) together with 2,2-dichloropropane, b.p. 70° [illegible] from acetone (1:5400) + PCl_5 see (6) (7) [illegible] KOH (3) or [illegible] from 1,2-dic[illegible] with cyclop[illegible] [illegible]propane (3:5450) + 1,2,2-trichloroprop[illegible] [illegible]ment with Zn see (14).]

$\bar{C}$ with MeOH forms a const.-boilg. mixt., b.p. 22.0°, contg. 97% $\bar{C}$ + 3% MeOH (15).

$\bar{C}$ treated with conc. H_2SO_4 and (after evoln. of HCl has ceased) poured into much aq. and steam-distd. (16) or $\bar{C}$ htd. with 10 vols. aq. in s.t. at 140–180° (17) yields acetone (1:5400) q.v.

$\bar{C}$ adds Br_2 yielding (8) (12) 2-chloro-1,2-dibromopropane [Beil. I-111], b.p. 169–170° cor (12).

$\bar{C}$ adds HBr fairly readily; in the presence of air or of antioxidants in vacuo, the product is pure 2-chloro-2-bromopropane, b.p. 91.0–92.0° at 740 mm., 34.6–34.8° at 100 mm., n_D^{20} = 1.4575 (4), in the presence of organic peroxides the major reactn prod. is 2-chloro-1-bromopropane, b.p. 117.6–118.0° at 740 mm, 52.2–52.8° at 75 mm., n_D^{20} = 1.4778 (4).

3:7020 (1)
mermans, *B*
178 (1940).
Ann. **138**, 1
Weidenbaur
Friedel, *An*
(11) Gou
14, 462–464 (1878). (13) Young (to Carbide and Carbide Corp.), U.S. 1,752,049, March 25, 1930; *Cent.* **1930**, II 1280. (14) Hass, Hinds (to Purdue Research Foundation), U.S. 2,235,762, March 18, 1941; *C.A.* **35**, 4042 (1941). (15) Lecat, *Rec. trav. chim.* **46**, 242 (1927). (16) Oppenheim, *Ann. Suppl.* **6**, 364–366 (1868). (17) Linnemann, *Ann.* **161**, 66 (1872).

3:7022 ETHYL HYPOCHLORITE $CH_3.CH_2OCl$ C_2H_5OCl Beil. I - 324
I_1-(164)
I_2-(325)

B.P. 36° at 758 mm. (1) **D^{-6}_{4} = 1.013 (1)**
36° at 752 mm. (2)

[*See also ter-butyl hypochlorite* (3:7165).]

Colorless oil (rapidly turning yellow in light) with odor like hypochlorous acid. — $\bar{C}$ explodes on superhtg. its vapor or even in cold upon addn. of Cu powder or in bright sunlight — $\bar{C}$ gradually decomposes on stdg. in diffuse light with formn. of ethyl acetate and other prods. (3) (4) (10). [For study of stability of $\bar{C}$ in aq. or in CCl_4 soln. see (4).] — Sol. ether, C_6H_6, $CHCl_3$; for distrib. of $\bar{C}$ between aq. and CCl_4 see (4).

[For prepn. of $\bar{C}$ from EtOH (1:6130) with Cl_2 in cold aq. alk. (2) (5) (1) (6) (7) (8) (9) or alk. earth (9) or with aq. HOCl in pres. of CCl_4 (4) see indic. refs.; for formn. of $\bar{C}$ from EtOH (1:6130) with Cl_2 at −18° (8) or with dry $Ca(OCl)_2$ (15) or aq. HOCl (15) (16) see indic. refs.]

$\bar{C}$ is able according to prevailing circumstances to act as an oxidizing agent, chlorinating agent, or for addn. to unsaturated linkages: furthermore since in aq. $\bar{C}$ is extensively hydrolyzed (69% in sat. aq. soln. (4)) it may serve as source of HOCl; examples of these reactions are given below.

$\bar{C}$ with inorganic reactants. $\bar{C}$ with KI + AcOH liberates I_2 quant. according to the equation $C_2H_5OCl + 2HI \rightarrow C_2H_5OH + HCl + I_2$ (use in quant. detn. of $\bar{C}$ (2) (4) (7)); $\bar{C}$ with dil. alk. Na_3AsO_3 gives (11) (12) EtCl (3:7015) + Na_3AsO_4; $\bar{C}$ in dil. alk. KSH/KCN mixt. gives (12) KSCN + KCl + EtOH.

[$\bar{C}$ adds to dry SO_2 yielding (5) ethyl chlorosulfonate [Beil. I-327, I_2-(327)], b.p. 151–154° dec., n_D^{18} = 1.4174]

[$\bar{C}$ (1 mole) with KCN (2 moles) in 7 pts. aq. at −5° gives (30% yield (13)) ethyl cyanoiminoformate [Beil. II-549, II_1-(238), II_2-(511)], oil, b.p. 133° dec., accompanied by a little diethyl di-imino-oxalate [Beil. II-547, II_1-(238)], m.p. 38°, b.p. 172° strong dec.; in aq. alc., however, the same components give (13) diethyl iminocarbonate [Beil. III-37, III_1-(18), III_2-(31)], oil, b.p. 141° cor., accompanied by diethyl di-iminooxalate (see above).]

$\bar{C}$ with organic reactants. [$\bar{C}$ with EtOH (1:6130) yields (8) acetaldehyde (1:0100), acetaldehyde diethylacetal (1:0156), and paraldehyde (1:0170). — $\bar{C}$ with acetaldehyde (1:0100) at 0° followed by distn. of the mixture with anhyd. oxalic acid yields (3) chloroacetaldehyde (3:7212).]

[$\bar{C}$ with acetone (1:5400) yields (3) chloroacetone (3:5425); $\bar{C}$ with methyl phenyl ketone (acetophenone) (1:5515) yields (3) ω-chloroacetophenone (phenacyl chloride) (3:1212); $\bar{C}$ with benzaldehyde (1:0195) yields (3) benzoyl chloride (3:6240).]

[$\bar{C}$ with phenol in CCl_4 yields (3) both *o*-chlorophenol (3:5980) and *p*-chlorophenol

(3:0475); C̃ with hydroquinone (1:1590) in ether gives (3) 2,3-dichlorohydroquinone (3:4220).]

C̃ with phenyl MgBr in ether at 0° gives (60% yield (14)) (1) chlorobenzene (3:7903).

[C̃ with phenylacetylene (1:7425) in CCl_4 yields (3) ω,ω-dichloroacetophenone (3:6835).]

[C̃ with cyclohexene (1:8070) in CCl_4 yields (3) 2-chlorocyclohexanol-1 (3:0175); for reactn. of C̃ with indene (1:7522) or with 1,4-dihydronaphthalene see (3).]

[C̃ with olefins adds to the unsatd. linkage to give chlorohydrin ethyl ethers (a process now generically designated as chloroalkoxylation): e.g., C̃ with ethylene yields (15) (17) β-chloroethyl ethyl ether (ethylene chlorohydrin ethyl ether) (3:7463); C̃ with amylene gives (3) a corresp. prod.; the rate of addn. of C̃ to olefins increases from ethylene to amylene (18). — For extensive studies on the prepn. of chlorohydrin ethers from olefins by use of alcs. + *N,N*-dichlorobenzenesulfonamide (which mixture appears to generate ROCl as the active addn. agent) see (18) (19) (20) (21).]

[C̃ has, however, but slight tendency to add to unsaturated acids: e g., C̃ in CCl_4 has no actn. (22) on cinnamic acid (1:0735); C̃ in dry ether or CCl_4 with crotonic acid (1:0425) or sorbic acid gives only traces (23) of the expected prods. — C̃ in CCl_4 with hexen-3-oic acid-1 (hydrosorbic acid) [Beil. II-435, II_1-(193), II_2-(404)] gives addn. to extent of 92% in 3 days (23), but the prod. is not a chloro-ethoxy-hexanoic acid and consists entirely of a mixt. of two stereoisomeric β-chlorohexanoic lactones.]

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3:7025 2-CHLOROPROPANE (Isopropyl chloride)

$$CH_3—\underset{H}{\overset{Cl}{C}}—CH_3$$

C_3H_7Cl Beil. I - **105**, I_1-(**34**), I_2-(**72**)

B.P.		F.P.		
36–37°	(1)	**−117.0°** (8)	D_4^{25} = **0.84281** (8)	
36.5° at 760 mm.	(2) (5)		D_4^{20} = **0.86168** (8)	n_D^{20} = **1.377** (17)
36.2–36.5° u.c.	(3)		**0.8610** (7)	
36.25°	(4)		D_4^{15} = **0.86797** (8)	n_D^{15} = **1.38110** (8)
36.0° at 760 mm.	(6)			
35.5° at 757 mm.	(7)			
34.8 at 760 mm.	(8)			
34.5° at 740 mm.	(43)			

Colorless limpid liquid with not unpleasant odor. — Alm. insol. aq. [for precise data see (9) (10) (11).] — [For use as refrigerant see (12).]

$\bar{C}$ with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 33.4°, contg. 94 wt. % $\bar{C}$ (4); $\bar{C}$ with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 35.6°, contg. 97.2 wt. % $\bar{C}$ (4) [*for other azeotropes see* Beil. I_2-(72).]

[For prepn. of $\bar{C}$ from propanol-2 (1:6135) with conc. HCl + $ZnCl_2$ (yield: 70–76% (13)) (14) (15) (16) (17) (43); with PCl_3 + $ZnCl_2$ (74% yield (15)); with PCl_5 + $ZnCl_2$ (66% yield (15)); with $SOCl_2$ + pyridine (80% yield (15)); or with $AlCl_3$ (70% yield (18)) see indic. refs.; for prepn. from propylene by addn. of HCl under various conditions see (19) (20) (21) (22) (23) (24) (25) (26) (27) (28) (29) (30).]

[For formn. of $\bar{C}$ (together with other products) by actn. of Cl_2 on propane see (31), for further actn. of Cl_2 on $\bar{C}$ see (3).] — [For isomerization of 1-chloropropane to $\bar{C}$ in presence of metallic catalysts see 1-chloropropane (3:7040).] — [For purification of $\bar{C}$ with conc. H_2SO_4 see (32).]

$\bar{C}$ on hydrolysis yields propanol-2 (1:6135). [For study of this reactn. see (2); for use in mfg. of propanol-2 see (33).]

[For reactn. of $\bar{C}$ with KI in acetone see (1).]

$\bar{C}$ with Mg in dry ether gives (90% yield (17), 93.9% (44)) RMgCl (for reactions of this see below).

[For study of behavior of $\bar{C}$ with C_6H_6 or toluene in pure HCl under press. see (45); for behavior with C_6H_6 + Al/Hg see (46).]

Ⓓ **Isobutyranilide**: m.p. 105° (34); 104–105° (35); u.c. (36); 103° cor. (37). [From $\bar{C}$ (36) or from isopropyl bromide (37) via conversion to RMgX and reactn. with phenyl isocyanate.]

—— ***Isobutyr-p-toluidide***: *m.p. 108.5–109.5° (38); 106–106.5° (39).* [Presumably similarly obtainable via RMgCl + *p*-tolyl isocyanate but not actually so recorded.]

—— **Isobutyr-α-naphthalide**: unrecorded.

—— ***S*-(Isopropyl)isothiourea picrate**: m.p. 196° (40). [From isopropyl bromide on htg. 3 hrs. in alc. with thiourea, then adding PkOH (40), but not recorded from $\bar{C}$.]

—— **Isopropyl mercuric chloride (*sec*-PrHgCl)**: m.p. 97° (47). [Reported only by indirect means (47).]

—— ***N*-(Isopropyl)phthalimide (2-(*N*-phthalimido)propane)**: m.p. 86° (48), 85° (49). [Not reported from $\bar{C}$ but obtd. from isopropyl bromide with K phthalimide in *s.t.* at 160–170° for 7 hrs. (49), also indirectly (48) (50).]

—— ***N*-(Isopropyl)-3-nitrophthalimide**: unreported.

—— ***N*-(Isopropyl)tetrachlorophthalimide**: unreported.

—— ***N*-(Isopropyl)-*o*-sulfobenzoic imide(*N*-isopropylsaccharin)**: m.p. 134° (51). [Not reported from $\bar{C}$ but obtd. from either isopropyl bromide or isopropyl iodide with aq. sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 mm. (51).]

—— ***N*-(Isopropyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine**: m.p. 107° u.c. (52). [Not reported from $\bar{C}$ but obtd. from isopropyl bromide with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine in alc. KOH (52).]

—— ***p*-Isopropoxybenzoic acid**: m.p. 160–163° (53). [From $\bar{C}$ (?) or from isopropyl bromide with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (53).]

—— **Isopropyl 2,4,6-triiodophenyl ether**: m.p. 43° cor. (41). [From isopropyl bromide on refluxing with 2,4,6-triiodophenol, m.p. 157–158°, in alc. NaOEt (41).]

—— **Isopropyl α-naphthyl ether**: b.p. 282.5° cor. (42) [picrate: m.p. 104.5–105.5° cor. (42)].

—— Isopropyl β-naphthyl ether: b.p. 285° cor., m.p. 40.0° cor. (42) [picrate: m.p. 95.0–95.5° cor. (42)].

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3:7030 1-CHLOROPROPENE-1 (Propenyl chloride, β-methylvinyl chloride)

$CH_3.CH{=}C(H)Cl$ C_3H_5Cl Beil. I - 198, I_1—, I_2—

trans form

B.P.	F.P.	
37.4° at 760 mm. (1)	**−99° (1)**	n_D^{20} = **1.4054 (2)**
36.7° at 747 mm. (2)		

cis form

B.P.	F.P.	
32.8° at 760 mm. (1)	**−134.8° (1)**	n_D^{20} = **1.4053 (2)**
32.0–32.2° at 747 mm. (2)		

Mobile colorless liq. lighter than water (3). $\bar{C}$ is stable toward hydrolysis; for use in anal. of mixts. of $\bar{C}$ with 3-chloropropene-1 (allyl chloride) (3:7035) see (7).

[For prepn. of $\bar{C}$ from 1,1-dichloropropane (3:7230) + alc. KOH in s.t. at 100° (3) (4) or with alc. NaOEt (2) see indicated refs.; for formn. from 1,2-dichloropropane (propylene dichloride) (3:5200) + alc. KOH see (3) (5) ($\bar{C}$ is principal product (5), but some 2-chloropropene-1 (3:7020) and propadiene are also formed); for formn. of *cis* isomer from α,β-dichloro-*n*-butyric acid of m.p. 62.5–63° by warming with Na_2CO_3 see (6).]

$\bar{C}$ with Br_2 at −15° yields 1-chloro-1,2-dibromopropane, b.p. 177–177.5° cor. (3).

$\bar{C}$ in presence of air or added peroxides adds HBr rapidly to give exclusively (2) 1-chloro-2-bromopropane, b.p. 117.2–117.3° at 740 mm., 52.0° at 75 mm., n_D^{20} = 1.4795 (2).

[For study of molecular refraction and dipole moment of both *cis* and *trans* forms of $\bar{C}$ see (8).]

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3:7035 3-CHLOROPROPENE-1 (Allyl chloride)

$CH_2{=}CH.CH_2Cl$ C_3H_5Cl Beil. I - 198; I_1-(82); I_2-(169)

B.P.			F.P.		
46.0–47.5° at 772.5 mm.	**(1)**		**−134.5°** **(7)**	D_4^{25} = **0.93109 (7)**	
46–47° at 758 mm.	**(2)**		**−136.4° (10)**		
46.0–46.5°	**(3)**			D_4^{20} = **0.9379 (14)**	
46°	**(4)**			**0.93764 (7)**	
45.7° at 760 mm.	**(5)**			**0.9374 (11)**	
45.5–47° at 756.9 mm.	**(1)**			**0.9267 (9)**	
45.36°	**(6)**			D_4^{15} = **0.94410 (7)**	
45.1° at 760 mm.	**(7)**				
44.9° at 751 mm.	**(108)**				n_D^{20} = **1.41538 (14)**
44.8–45.0° at 756.2 mm.	**(8)**	**(61)**			**1.4151 (11)**
44.8° at 754 mm.	**(9)**				**1.40950 (9)**
44.6° at 760 mm.	**(10)**				
44.6°	**(11)**	**(12)**			n_D^{15} = **1.41883 (7)**
44.5–44.7° at 744 mm.	**(13)**				
44.4–44.6°	**(14)**				

Colorless oil, spar. sol. aq.; volatile with steam.

$\bar{C}$ with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 44° at 760 mm., contg. 95% $\bar{C}$ (5); with formic acid (1:1005) forms a const.-boilg. mixt., b.p. 45.0° at 760 mm., contg. 92.5% $\bar{C}$ (15).

$\bar{C}$ is one of most toxic of all halohydrocarbons (for study see (16)).

[For prepn. of $\bar{C}$ from allyl alcohol (1 [illegible] in s.t. at 100° for 3 hrs. (17), with conc. HCl [illegible] (1) (23) or 10 days at room temp. (55–6 [illegible] 6 *N* HCl (50% yield (19)), with $ZnCl_2$ [illegible] or dislvd. in cold conc. HCl and treated with Cu_2Cl_2 (small amt.) + conc. H_2SO_4 (yield 85–90% (2), 80% (22)) see indic. refs.; from allyl alcohol (1:6145) with $SOCl_2$ in C_6H_6

(71% yield (21)), with PCl_3 (1) (24), with $PCl_3 + ZnCl_2$ in C_6H_6 at 0° (63% yield (21)), with PCl_3 + pyridine (73% yield (9)), with $PCl_5 + ZnCl_2$ in C_6H_6 (57% yield (21)) see indic. refs.]

[For prepn. of $\bar{C}$ from allyl formate (1:3035) with conc. HCl + a little Cu_2Cl_2 + conc. H_2SO_4 (93–98% yield (22)), or with $ZnCl_2$ + HCl gas (80–90% yield (25)) (26) see indic. refs.; from allyl oxalate in alc. $CaCl_2$ in s.t. at 100° see (27); from allyl iodide with alc. $HgCl_2$ at ord. temp. see (27).]

[For comml. prepn. of $\bar{C}$ from propylene with Cl_2 at elevated temps., e.g., 500° (yield 96% $\bar{C}$ accompanied by 3% 2-chloropropene-1 (3:7020) + 1% mixed *cis* and *trans* isomers of 1-chloropropene-1 (3:7030) (11)) (28) (29), see indic. refs. (note also that the high-boiling material from distn. of comml. $\bar{C}$ contains (110) approx. 60% 1,3-dichloropropene-1 (3:5280) + 30% 1,2-dichloropropane (3:5200)); for examples of patents covering this procedure see (30) (31) (32) (33) (34) (35), from propane (34) (36) or 1-chloropropane (3:7040) (36) with Cl_2 + cat. at 500–700° see indic. refs.; from 1,2-dichloropropane (3:5200) by suitable pyrolysis (yield: 55–70% $\bar{C}$ + 30–40% of mixt. of *cis* and *trans* isomers of 1-chloropropene-1 (3:7030) + 5% 2-chloropropene-1 (3:7020) (11)) cf. (12) (13) (39); for examples of relevant patents see (37) (38) (40).]

Reactions involving the double bond of $\bar{C}$. [$\bar{C}$ with Cl_2 adds and/or substitutes according to conditions (for study of relative proportions of these reactions see (29) (11)); $\bar{C}$ with Cl_2 at ord. temp. (41) or $\bar{C}$ with SO_2Cl_2 in CCl_4 in pres. of peroxides (42) gives (80–90% yield (42)) 1,2,3-trichloropropane (3:5840) (note that this comprises one step in one of the modern syntheses of glycerol from petroleum (43) (44)); $\bar{C}$ with Cl_2 at high temp. yields (11) a mixt. of prods. of which the dichloropropene fraction comprises (11) 47% 1,3-dichloropropene-1 (high-boilg. isomer) (3:5280) + 42% 1,3-dichloropropene-1 (low-boilg. isomer) (3:5280) + 11% 1,1-dichloropropene-2 (3:5140) + trace of 1,2-dichloropropene-2 (3:5190).]

[$\bar{C}$ with Br_2 adds 1 mole of halogen yielding (45) mainly 1,2-dibromo-3-chloropropane (γ-chloropropylene dibromide) [Beil. I-111], b.p. 195° (45); for study of rate of addn. of Br_2 under various conditions see (14) (9) (46) (105); for heat of reactn. see (47).]

[$\bar{C}$ with conc. aq. HCl in s.t. at 100° for 18 hrs. (48), or $\bar{C}$ with dry HCl in dark at 0° in absence of $FeCl_3$ (33% yield (49)) or at room temp. in pres. of $FeCl_3$ (85–89% yield (49)), gives 1,2-dichloropropane (propylene dichloride) (3:5200); note that addn. of HCl is not complicated by a peroxide effect but is very slow unless $FeCl_3$ (or less advantageously $AlCl_3$) is used as a cat. (49). — $\bar{C}$ satd. with HBr gas at 0° or below (50), or with conc. aq. HBr at 0° (51), or with HBr gas in s.t. at 100° for 8 hrs. (48) cf. (52), or in presence of Fe (53) or other cat., e.g., $BiCl_3$ (54), as directed, gives (yields: 36–38% (53), 43% (52), 50% (51), 87% (50)) 1-bromo-3-chloropropane (γ-chloro-*n*-propyl bromide) (trimethylene chlorobromide) [Beil. I-109, I_1-(36), I_2-(75)], b.p. 142°; note that the above mode of addn. is favored by peroxides (49) (54) cf. (106). — $\bar{C}$ with HI (10–20% excess at 0°) gives exclusively (90–100% yield (55)) 1-chloro-2-iodopropane, b.p. 66.2° at 50 mm., $n_D^{20} = 1.5472$ (55); note that in this reactn. formn. of 2-iodopropane (isopropyl iodide) has also been reported (56).]

[$\bar{C}$ (1 mole) with conc. H_2SO_4 (2 moles) at 0° gives an oily addn. prod. (24) (presumably β-chloroisopropyl hydrogen sulfate) which upon dilution with aq. and subsequent distillation gives (50% yield (57) (61)) (24) (58) (59) (60) 1-chloropropanol-2 (3:7747); in pres. of $CuSO_4$ the yield rises to 66–70% (62). — $\bar{C}$ adds HOCl yielding (63) (64) (65) (76) 2,3-dichloropropanol-1 (glycerol β-dichlorohydrin) (3:6060). — $\bar{C}$ with *ter*-butyl hypochlorite (3:7165) in MeOH contg. a little *p*-toluenesulfonic acid gives at 40° (44% yield (66)) 1,3-dichloro-2-methoxypropane (β,β'-dichloroisopropyl methyl ether), b.p. 154–156° at 730 mm., $D_4^{20} = 1.2235$, $n_D^{20} = 1.4542$ (66).]

[$\bar{C}$ with liq. SO_2 + trace of ascaridole + a few drops of aq. or alc. HCl, HBr, or H_2SO_4 gives (70–100% yield (67)) cf. (68) allyl chloride polysulfone, no def. m.p., dec. 210–235°, sol. $CHCl_3$ or acetone but insol. most other org. solvents; note, however, that this addn. of SO_2 is completely inhibited by the pres. of as little as 5 mole % of allyl *bromide* or cinnamyl *bromide* (67). — $\bar{C}$ (2 moles) with S_2Cl_2 (1 mole) in s.t. at 100° for 6 hrs. deposits sulfur and yields (69) *bis*-(β,γ-dichloro-*n*-propyl) sulfide, pale yel. oil, b.p. 181–182° at 15 mm. (69); the same components maintained at room temp. for 10 days, however, deposit no sulfur and on distn. yield (69) *bis*-(β,γ-dichloro-*n*-propyl) *di*sulfide, b.p. 190° at 11 mm. (69).]

[$\bar{C}$ (2 moles) with cyclopentadiene (1 mole) (1:8030) in s.t. at 170–180° for 8 hrs. gives (74% yield on C_5H_6 (70)) by Diels-Alder addn. 2,5-endomethylene-1,2,5,6-tetrahydrobenzyl chloride (1-(chloromethyl)-2,5-endomethylenecyclohexene-3), b.p. 54–57° at 11 mm. (70). — For polymerization of $\bar{C}$ see (71) (101).]

[$\bar{C}$ with excess diazomethane in ether stood for 3 days yields a yel. very hygroscopic ppt. presumably 3-(chloromethyl)-Δ^2-pyrazoline (72).]

[$\bar{C}$ with C_6H_6 + conc. H_2SO_4 gives (73) by addn. to the ethylene linkage β-chloro-*n*-propylbenzene (2-chloro-1-phenylpropane) [Beil. V-391, V_1-(189), V_2-(304)], b.p. 85° at 13 mm., D_{-}^{19} = 1.047, n_D^{19} = 1.5245 (73); note, however, that $\bar{C}$ with C_6H_6 in pres. of $FeCl_3$ at −20° gives (33.5% yield (74)) (73) the isomeric (β-chloroisopropyl)benzene (1-chloro-2-phenylpropane) [Beil. V_1-(191)], b.p. 79° at 10 mm., D_4^{17} = 1.0367, n_D^{18} = 1.52129 (74); $\bar{C}$ with C_6H_6 + $AlCl_3$ (⅙ mole) gives none of the β-chloroisopropylbenzene since it apparently reacts with more C_6H_6 yielding (74) α-methylbibenzyl (1,2-diphenylpropane [Beil. V-613, V_1-(288), V_2-(517)].] [For analogous condensation of $\bar{C}$ with fluorobenzene, chlorobenzene (3:7903), and bromobenzene see (118).]

[For oxidn. of $\bar{C}$ in liq. phase at 75–250° by O_2 in pres. of $Cu(OAc)_2$ or peroxide catalysts and in an org. solv. such as AcOH to hydroxylated cpds. see (75).]

Reactions involving the halogen atom of $\bar{C}$. [$\bar{C}$ + H_2 over activated charcoal at 300–500° gives (58% yield (77)) propylene; note that the double bond is *not* (77) hydrogenated.]

[$\bar{C}$ passed over activated charcoal contg. 1–2% KOH is dehalogenated (78) at 375° to extent of 21%; at 400°, 58%.]

[$\bar{C}$ with aq. vapor at 550–850° + cat. (79) or under press. with alkali hydroxides (80) or with HCl/Cu_2Cl_2 (108) yields (cf. (43) (44)) allyl alcohol (1:7145). — $\bar{C}$ with alc. KOH (81) (107) or alc. NaOH (12) yields allyl ethyl ether (1:7850) + alkali chloride; for use of this reactn. in detn. of $\bar{C}$ in pres. of *cis*-1-chloropropene-1 (3:7030) and *trans*-1-chloropropene-1 (3:7030) see (12); for study of rate of reactn. of $\bar{C}$ with NaOMe at 16–18° (82) or of $\bar{C}$ with NaOEt at 35° and 50° (83) see indic. refs.]

[$\bar{C}$ with alc. KSH gives mainly (84) di-allyl sulfide [Beil. I-441, I_1-(226), I_2-(478)], b.p. 138–139° (84).] — [For reactn. of $\bar{C}$ with alkali polysulfides in prepn. of rubber-like prod. see (85).]

[*For studies of rate of reactn. of* $\bar{C}$ *with KI in acetone at 20° (83), 25° (86), or 60° (87)* cf. (9) see indic. refs.; for reactn. of $\bar{C}$ with Na_3AsO_3 yielding allylarsinic acid see (88); for reactn. of $\bar{C}$ with CuCN giving (85% yield (22)) allyl cyanide (vinylacetonitrile) [Beil. II-408, II_1-(187), II_2-(389)], b.p. 117.8–118.2° at 757 mm. (22), see indic. refs.; for reactn. of $\bar{C}$ with Mg + acetone, giving allyl-dimethyl-carbinol [Beil. I-445, I_2-(487)], b.p. 118–120°, D_4^{17} = 0.83452, n_D^{17} = 1.4300 see (89).]

[$\bar{C}$ with conc. aq. NH_4OH as directed (90) yields allylamine [Beil. IV-205, IV_1-(389), IV_2-(662)], b.p. 56°, misc. aq. — For study of rate of addn. of $\bar{C}$ to pyridine or reactn. with piperidine see (82) (91); for sepn. of $\bar{C}$ from other chloro-olefins, e.g., 1-chloropropene-1 (3:7030) or 2-chloropropene-1 (3:7020), by conv. of $\bar{C}$ to quaternary salt see (111).]

$\bar{C}$ with Mg in dry ether under carefully regulated conditions gives (84% yield (102))

cf. (109) (119) allyl MgCl; note that if this prod. reacts with phenyl isocyanate in a fashion analogous (103) to allyl MgBr the prod. obtd. should be crotonanilide, m.p. 113–114° cor. (103).

[$\bar{C}$ with Mg in dry ether as directed gives (68% yield crude, 27% pure (92), 60% (93)) hexadiene-1,5 (1:8045). — $\bar{C}$ with $NaNH_2$ in liq. NH_3 as directed gives (30% yield (94)) hexatriene-1,3,5 [Beil. I-263, I_1-(243)], b.p. 76–80°, $D_4^{20} = 0.7182$, $n_D^{20} = 1.4330$ (94); during the reactn. an intermediate chlorohexadiene (95), b.p. 115° at 748 sl. dec., 46–47.5° at 96 mm., $n_D^{20} = 1.4483$, appears to be formed, and the hexatriene is accompanied (94) (95) by variable amts. of its dimer, trimer, and tetramer. — For reaction of $\bar{C}$ with monosodium acetylene in liq. NH_3 see (96).]

[$\bar{C}$ with 1-chloro-2-methylpropene-2 (methallyl chloride) (3:7145) + Mg in ether gives (93) 47% 2-methylhexadiene-1,5 (b.p. 88.1° at 760 mm., $D_4^{20} = 0.7198$, $n_D^{20} = 1.4184$) + 30% 2,5-dimethylhexadiene-1,5 (b.p. 114.3° at 760 mm., $D_4^{20} = 0.7423$, $n_D^{20} = 1.4293$) + 12% hexadiene-1,5 (biallyl) (1:8045). — $\bar{C}$ with crotyl chloride (the equil. mixt. of 1-chlorobutene-2 (3:7205) and 3-chlorobutene-1 (3:7090)) + Mg in ether gives 34% heptadiene-1,5 (b.p. 93.7° at 760 mm., $D_4^{20} = 0.7186$, $n_D^{20} = 1.4200$) + 21% 3-methylheptadiene-1,5 (b.p. 111.0° at 760 mm., $D_4^{20} = 0.7291$, $n_D^{20} = 1.4240$) + 10% hexadiene-1,5 (1:8045) + 10% 3-methylhexadiene-1,5 (b.p. 80.0° at 760 mm., $D_4^{20} = 0.7103$, $n_D^{20} = 1.4116$) + 1% octadiene-1,6 (b.p. 124.5° at 760 mm., $D_4^{20} = 0.7441$, $n_D^{20} = 1.4336$) (93).]

[$\bar{C}$ reacts with RMgX cpds. in normal coupling; e.g., $\bar{C}$ with EtMgBr gives (97) pentene-1 (1:8205); $\bar{C}$ with n-PrMgBr gives (97) hexene-1 (1:8255); $\bar{C}$ + n-C_5H_{11}MgCl gives (80% yield (93)) octene-1 (1:8375); $\bar{C}$ with iso-AmMgCl gives (60% yield (93)) 6-methylheptene-1 (b.p. 113.2° at 760 mm., $D_4^{20} = 0.7119$, $n_D^{20} = 1.4068$); $\bar{C}$ with o-tolyl MgBr gives (98) o-allyltoluene (b.p. 182–183° at 757 mm., $D_4^{20} = 0.9001$, $n_D^{20} = 1.5186$).]

Miscellaneous reactions of $\bar{C}$. [$\bar{C}$ with phenol (1:1420) + conc. H_2SO_4 stood at room temp. for 6 months gives (99) o-isopropenylphenol [Beil. VI-572, VI_1-(283)]; for analogous prods. from $\bar{C}$ with o-cresol (1:1400), m-cresol (1:1730), and p-cresol (1:1410) see (99).]

Ⓓ *S*-**Allylisothiurea picrate**: m.p. 155° (100). [From $\bar{C}$ thiourea in EtOH, refluxed for 5 min., treated with PhOH (100).]

—— *N*-**(Allyl)phthalimide** [Beil. XXI-464, XXI_1-(364)]: m.p. 70°. [The direct prepn. of this cpd. from $\bar{C}$ has not been reported; it has, however, been obtd. from allyl bromide with K phthalimide in s.t. at 150° for 2–3 hrs. (50% yield (104)) and has also been prepd. by numerous indirect means; with Cl_2 in $CHCl_3$ it yields N-(β,γ-dichloro-n-propyl)phthalimide, ndls. from alc., m.p. 93° (104); with Br_2 in $CHCl_3$ it yields N-(β,γ-dibromo-n-propyl)phthalimide, m.p. 113–114° (104).]

—— *N*-**(Allyl)-3-nitrophthalimide**: pl. from CS_2, m.p. 100–101° (112). [Not reported from $\bar{C}$ but obtd. from allyl bromide with K 3-nitrophthalimide (112), for photographs of cryst. see (113).]

—— *N*-**(Allyl)tetrachlorophthalimide**: unreported.

Ⓓ *N*-**(Allyl)-o-sulfobenzoic imide** (*N*-**allylsaccharin**): m.p. 58° (114). [From $\bar{C}$ with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (114).]

—— *N*-**(Allyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide**: m.p. 82° u.c. (115). [Not reported from $\bar{C}$ but obtd. from allyl bromide with N-(p-bromobenzenesulfonyl)-p-anisidine in alc. KOH (115).]

—— *p*-**Allyloxybenzoic acid**: m.p. 162–163° u.c. (116). [From $\bar{C}$ (?) or from allyl bromide with ethyl p-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (116); note, however, that m.p. of prod. is almost identical with corresp. deriv., m.p. 160–163°, from isopropyl halides.]

—— Allyl α-naphthyl ether: m.p. −10° (117) (corresp. picrate, m.p. 100.5–101.0° cor. (117)).

—— Allyl β-naphthyl ether: m.p. +16° (117) (corresp. picrate, m.p. 98.5–99.0° cor. (117).)

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3:7040 1-CHLOROPROPANE $CH_3.CH_2.CH_2Cl$ C_3H_7Cl Beil. I - **104**
(*n*-Propyl chloride) I_1- (34)
I_2- (72)

B.P.				F.P.		
46.60°	at	760 mm.	(1)	**−122.8°** (1) (7)	D_4^{25} = **0.88611**	(1)
46.6°	at	770.5 mm.	(2)		D_4^{20} = **0.89229**	(1)
46.3–46.7° u.c.			(3)		**0.8890**	(52)
46.4° cor.	at	760 mm.	(4) (5)		D_4^{15} = **0.89486**	(1)
46.0–46.5°	at	764 mm.	(52)		n_D^{20} = **1.38856**	(8)
45.70–45.75°	at	760 mm.	(6)		**1.38838**	(9)
44°	at	744 mm.	(8)		**1.38800**	(52)

Colorless limpid liquid with not unpleasant odor. — Almost insol. aq. [for precise data see (10) (11) (12)].

$\bar{C}$ with MeOH, b.p. 64.7°, forms const.-boilg. mixt., b.p. 40.5°, contg. 90.5 wt. % $\bar{C}$ (13); $\bar{C}$ with EtOH, b.p. 78.3°, forms const.-boilg. mixt., b.p. 45.0°, contg. 94 wt. % $\bar{C}$ (14); $\bar{C}$ with isopropyl alc., b.p. 82.5°, forms const.-boilg. mixt., b.p. 46.4°, contg. 97.2 wt. % $\bar{C}$ (14); $\bar{C}$ with CS_2, b.p. 46.3°, forms const.-boilg. mixt., b.p. 42.05°, contg. 44.5 wt. % $\bar{C}$ (14). — [For f.p./compn. data on mixts. of $\bar{C}$ with cyclohexyl chloride (3:8040) or with isopropyl bromide see (15).]

[For prepn. of $\bar{C}$ from propanol-1 (1:6150) with con- HC . Z-C ...
70–72% (16), 65–70% (17), 61% (18) (19)); with PCl_3 (2 ...
with PCl_5 (5) + $ZnCl_2$ (76% yield (19)); with $SOCl_2$ + ...
refs.; for other misc. methods see Beil.]

[For formn. of $\bar{C}$ (togeth ...
for further actn. of Cl_2 on ...

[For isomerization of $\bar{C}$ ...
(28); for isomerization of $\bar{C}$ accompanying alkylation see (29); for $\bar{C}$ in Friedel-Crafts reactn. see (30).]

$\bar{C}$ on passing over various cat. espec. at elevated temps. loses HCl (30) (31) + Beil. I_2-(72).

[For study of behavior of $\bar{C}$ with KI see (33); toward Na see (34) (35) (36); with Mg in dry ether see (37) (note that $\bar{C}$ with Mg in dry ether contg. trace of I_2 gives in absence of air 98.2% yield (51) RMgCl).]

Ⓓ *n*-**Butyranilide**: m.p. 96° (38); 97° (39); 92° cor. (40), u c. (41). [From $\bar{C}$ (41) or *n*-propyl bromide (40) via conversion to RMgX and reactn. with phenyl isocyanate (41).]

—— *n*-**Butyr-*p*-toluidide**: m.p. 75° (38); 74–75° (42); 73–74° (43). [Presumably similarly obtainable via RMgCl + *p*-tolyl isocyanate, but not actually so recorded.]

Ⓓ *n*-**Butyr-α-naphthalide**: m.p. 120° (44); 121° (45). [From RMgBr via reactn. with α-naphthyl isocyanate (45).]

—— *n*-**Propyl mercuric chloride**: m.p. 140° (46).

Ⓓ *S*-(*n*-**Propyl)isothiourea picrate**: m p. 176° (47). [In small yield from $\bar{C}$ on htg. 5 hrs. with thiourea in alc., followed by addn. of PkOH (47).]

—— *n*-**Propyl 2,4,6-triiodophenyl ether**: m.p. 82° cor. (48). [From *n*-propyl bromide on *refluxing with 2,4,6-triiodophenol, m.p. 157–158°, in alc. NaOEt (48).]* [*Note* that this ether depresses m.p. of corresp. Et 2,4,6-triiodophenyl ether, m.p. 82° cor. (48).]

—— *N*-(*n*-**Propyl)-3-nitrophthalimide**: ndls. from CS_2, m.p. 84–85° (49). [From *n*-propyl bromide on refluxing with K 3-nitrophthalimide (49).]

—— *n*-**Propyl α-naphthyl ether**: b.p. 293.5° cor. (50) [picrate: m.p. 99.5–100° cor. (50)].

—— *n*-**Propyl β-naphthyl ether**: b.p. 297.0° cor., m.p. 39.5–40 0° cor. (50) [picrate: m.p. 80.5–81.5° cor. (50)].

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56, 2119 (1934). (42) Davis, *J. Chem. Soc.* **95**, ... *prakt. Chem.* (2) **74**, 323 (1906). (44) Robertson, ... (1928).
... *em.* ... Ma, ...
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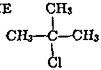
(51) Houben, Boedler, Fisch ... 43, 638–639.

3:7045 2-CHLORO-2-METHYLPROPANE C_4H_9Cl Beil. I - 125
(*ter*-Butyl chloride; I_1-(40)
trimethylcarbinyl chloride) I_2-(88)



B.P.			F.P.			
52°		(1)	−24.6°	(12)	D_4^{25} = 0.83537	(9)
51.52° cor.		(2) (36)	−25.4°	(13)	D_4^{20} = 0.8511	(20)
51.6°		(3)	−27.1°	(9) (19)	0.8457	(16)
51.0–51.2°		(4)	−28.5°	(5)	0.84138	(9)
51°		(5)			D_4^{15} = 0.84739	(9)
50.9°	at 762 mm.	(6)				
50.9°		(7)				
50.8°	at 766 mm.	(8)			n_D^{20} = 1.38786	(13)
50.7°	at 760 mm.	(9)			1.3858	(8)
50.7°		(10)			1.38564	(16)
50.6–50.8°	at 766 mm.	(11)			1.3855	(17) (21)
50.60°		(12) (18) (8)			1.3853	(8)
50.5°		(13)			1.38528	(10)
50.0°	at 749 mm.	(14)			1.38470	(12)
49.7°	at 742.4 mm.	(15)			1.3839	(18)
49.5°	at 738 mm.	(16)			n_D^{18} = 1.3860	(22)
49–50°		(17)			$n_D^{17.8}$ = 1.38686	(1)

[*See also 1-chloro-2-methylpropane* (3:7135).]

Binary systems of C̄ with other org. cpds. — For f.p./compn. data of mixts. of C̄ with CCl_4 (3:5100) (23) (13), with *n*-butyl chloride (3:7160) (19), with *n*-butyl bromide (19), or with isobutyl bromide (19) see indic. refs.

C̄ with MeOH (1:6120) forms a const.-boilg. mixt., b p. 43.75°, contg. 90% C̄ (24); C̄ with formic acid (1:1005) forms a const.-boilg. mixt , b.p. 50.0°, contg. 88.8% C̄ (3); C̄ with CS_2 forms a const.-boilg mixt., b.p. 43.3°, contg 37% C̄ (25). — Note that C̄ gives no azeotrope with *ter*-BuOH (1:6140) (9).

Preparation of C̄. [For prepn. of C̄ from *ter*-BuOH (1:6140) with conc. HCl (3 vols.) by shaking in cold (espec. in pres. of $CaCl_2$) (78–88% yield (26)) or by distillation (using

7–8 pts. by wt. conc. HCl) (94% yield (27)), or with dil. aq. HCl (18–20 Bé) in pres. of inorg. halide cat. (28) see indic. refs.]

[For prepn. of C̄ from *ter*-BuOH (1:6140) with dry HCl gas in cold (1) (29), with HCl gas in pres. of pyridine at elevated temp. (some isobutyl chloride (3:7135) is also formed (30)); with PCl_3 (31), $PCl_3 + ZnCl_2$ (92% yield (32)), PCl_5 (33) (34), $PCl_5 + ZnCl_2$ (85% yield (32)), or excess $AlCl_3$ (35); with oxalyl (di)chloride (3:5060) (36) or with trichloromethyl chloroformate (diphosgene) (3:5515) (20) see indic. refs.]

C̄ can also be obtained from various isobutyl cpds. (see following paragraphs), but it must be constantly kept in mind that reactns. of this type involve the equilibrium between *C̄, isobutylene, and isobutyl chloride, and the proportions of the two halides* may vary widely according to particular conditions; for some types of utilization, however, such a mixture may serve just as well as pure C̄.

[For prepn. of C̄ from 2-methylpropane (isobutane) with Cl_2 see (37) (38) (39); from isobutylene with HCl gas (40) (41) (4) (18), with conc. aq. HCl (42) (43) (44), with HCl gas + $AlCl_3$ at −50° (45), with HCl gas + cat. (46), from tech. cracked gas (contg. isobutylene) with HCl (47) (48) (49) (57), with chloromethyl methyl ether (3:7085) + $HgCl_2$ (other prods. are also formed (50)), or even with Cl_2 (other prods. also formed) (51) (52) (53) see indic. refs.]

[For prepn. of C̄ from 1-chloro-2-methylpropane (isobutyl chloride) (3:7135) by htg at 306° (8% C̄ (54)), or passing vapor over $BaCl_2$ at 380–400° (40% C̄ (55)), or over suitable cat. at 200° as directed (56); from isobutyl iodide with ICl (58); from isobutylamine with NOCl in xylene at −15° (59); from isobutyl alcohol (1:6165) with HCl gas (60) cf. (1), with HCl gas over Al_2O_3 at 420° (61), or with $PCl_3 + ZnCl_2$ (62) see indic. refs.]

[For formn. of C̄ from 2-chloro-2-methylbutane (*ter*-amyl chloride) (3:7220) by cleavage with $AlCl_3$ (35) or with anhydrous HF at 0° (10–17% yield (17)) see indic. refs.]

Pyrolysis of C̄. [C̄ on suitable htg. dec. into isobutylene + HCl; this begins to occur at 300° even in absence of cat. (63) (for study of equilibria involved see (4) (18)); for study of reactn. over ThO_2 at 100° (64), over pumice at 400–500° (65), or over activated carbon contg. 1–2% KOH (dehalogenation is 19.8% at 375°, 51% at 400° (66)) see indic. refs. — Note that C̄ passed over activated carbon at 400° in pres. of H_2 is 51% dehalogenated but the isobutylene is not reduced (67).]

Further halogenation of C̄. [C̄ in liq. phase with Cl_2 in light gives (68) a mixt. of chlorination prods. contg. approx. 37% 1,2,3-trichloro-2-methylpropane (3:5885) + 25% 1,1,2-trichloro-2-methylpropane (3:5710) + 21% 1,1,2,3-tetrachloro-2-methylpropane (3:6165) + 10% 1,2-dichloro-2-methylpropane (3:7430) + 6% 1,2,3-trichloro-2-(chloromethyl)-propane (3:6335) + a trace of 1,1,1,2-tetrachloro-2-methylpropane (3:4725). — C̄ in vapor phase under reduced press. with Cl_2 in u.v. light or in dark electric discharge (69) or C̄ with $SbCl_5$ (1 mole) with cooling (34) gives 1,2-dichloro-2-methylpropane (3:7430).]

C̄ with Br_2 in pres. of Fe (70) or in liq. SO_2 at room temp. for 14 hrs. (100% yield (72)) evolves HCl and gives 1,2-dibromo-2-methylbutane (isobutylene dibromide) [Beil. I-127, I_1-(41), I_2-(90)], b.p. 149.0°.

Reactions of the halogen atom of C̄. The tertiary chlorine atom of C̄ is very reactive and therefore readily hydrolyzed or alcoholized. — C̄ on shaking with aq. for 24 hrs. at room temp. (6) or C̄ on refluxing with 2 vols. aq. for 8 hrs. (71% hydrolysis (72)) yields *ter*-BuOH (1:6140); note rate of hydrolysis of C̄ is greater in pure aq. than in 5% aq. Na_2CO_3 (72); for use of this facile hydrolysis in removal of C̄ from isobutyl chloride (3:7135) see under latter). [For details of studies of kinetics of hydrol. of C̄ under various circumstances, e.g., in aq. alc., see (73) (74) (75) (6) (11); in formic acid (14) (77) (78).] [For use in prepn. of *ter*-butyl alc. (1:6140) see (79).]

[C̄ (2 moles) in ether shaken with Ag_2CO_3 (1 mole) gives (35% yield (114)) di-*ter*-butyl ether, b.p. 106.5–107°, $D_4^{20} = 0.7658$, $n_D^{20} = 1.3949$ (114).]

[$\bar{C}$ in the presence of small amts. $AlCl_3$ exchanges halogen with reactive H atoms of certain hydrocarbons; e.g., $\bar{C}$ with 2,3-dimethylbutane (1:8515) + $AlCl_3$ shaken for ½ min. at room temp. gives (23% yield (112)) 2-chloro-2,3-dimethylbutane (3:7600); $\bar{C}$ with 2,2,3-trimethylbutane (1:8544) + $AlCl_3$ shaken for 30–45 *seconds* gives (16% yield (112)) 3-chloro-2,2,3-trimethylbutane (3:4020); for other examples see (112).]

[$\bar{C}$ also undergoes alcoholysis: e.g., $\bar{C}$ shaken with equal vol. 50 mole % MeOH for several days (74) (11) seps. a non-aq. phase of *ter*-butyl methyl ether (1:7830), b.p. 55°; $\bar{C}$ with EtOH gives (11) *ter*-butyl ethyl ether (1:7860), b p. 73°; for study of this equilibrium and detn. of these ethers see (11).]

[For rate of reactn. of $\bar{C}$ with KI in acetone at 60° see (80); for reactn. of $\bar{C}$ with Ca formate yielding (77) (78) *ter*-butyl formate (1:3033), b.p. 83°, see indic. refs.; for conv. of $\bar{C}$ to esters by htg. with alkali salt of a suitable acid under press. at 125–225° in pres. of Cu and the use of this reactn. in sepn. of $\bar{C}$ from less reactive chlorine cpds. see (81).]

[$\bar{C}$ readily condenses with arom. hydrocarbons and phenols: e.g., $\bar{C}$ with Al/Hg + C_6H_6 gives (74.5% yield (109)) or $\bar{C}$ with C_6H_6 + $AlCl_3$ gives (yields: 69% (82), 60% (83)) (62) (1) mainly *ter*-butylbenzene (1:7460), b.p. 168.8°, often accompanied by some *p*-(di-*ter*-butyl)benzene, cryst. from alc., m p. 77° (82); this same condensation can also be effected in anhydrous HCl at 235° under press. (88% yield (84)) or in anhydrous HF (yield: 60% di- + 10% mono- (85)). — $\bar{C}$ with toluene + $AlCl_3$ gives *both* *p*-*ter*-butyltoluene and *m*-*ter*-butyltoluene (in ratio of 30–35/65–70, resp. (86)) but $\bar{C}$ with toluene in anhyd. HCl or HF (85) (22) cf. (113) gives exclusively (84) *p*-*ter*-butyltoluene, b p. 188–189°, n_D^{20} = 1.4930 (84). — For reactn. of $\bar{C}$ with naphthalene + $AlCl_3$ (87) or Al/Hg (109) or $\bar{C}$ with *m*-cymene + $AlCl_3$ (88) see indic. refs.]

[$\bar{C}$ with phenol (1:1420) in anhyd. HF gives (85% yield (89)) *p*-*ter*-butylphenol (1:1510); $\bar{C}$ with β-naphthol (1:1540) + $AlCl_3$ gives (90) 4-(*ter*-butyl)naphthol-2, m.p. 102° (90). — $\bar{C}$ with anisole (1:7445) + ZnF_2 gives (30.6% yield (91)) *p*-*ter*-butylanisole, but $\bar{C}$ does not react with anisole + AlF_3 or with furan + ZnF_2 (91).]

[$\bar{C}$ with acetanilide + $AlCl_3$ in ethylene dichloride at —10° gives (93% yield) *N*-acetyl-*p*-*ter*-butylaniline (111).]

$\bar{C}$ under proper conditions gives the corresponding RMgCl cpd.: e.g., $\bar{C}$ with Mg in dry ether as directed gives (yields: 80% (92), 62% (93), 60% (95)) cf. (94) *ter*-BuMgCl; this RMgCl cpd. undergoes the usual reactions (see also below under Ⓓ's) including the following: *ter*-BuMgCl with O_2 below 0° gives (80% yield (95)) *ter*-BuOH (1:6140) q.v.; with acetyl chloride (1 mole) in C_6H_6 gives (40–54% yield (92)) *ter*-butyl methyl ketone (pinacolone) (1:5425) (note, however, that *ter*-BuMgCl with excess acetyl chloride takes a different course (97) and that with various other acyl halides the reducing action of the *ter*-BuMgCl becomes conspicuous cf. (98) (99) (100)); $\bar{C}$ with ethyl chloroformate (3:7295) or diethyl carbonate (1:3150) gives (56% yield (92)) ethyl trimethylacetate (ethyl pivalate) (1:3117), with $\bar{C}$ itself to give (10% yield (96)) hexamethylethane (1:7090).

$\bar{C}$ reacts with other RMgX cpds. in conventional fashion: e.g., $\bar{C}$ with MeMgCl gives (42–50% yield (108)) tetramethylmethane (neopentane) (1:8499); $\bar{C}$ with *n*-PrMgBr in ether + $HgCl_2$ gives (yield 21% (101), 20% (110)) 2,2-dimethylpentane (1:8543); the numerous other reactions of *ter*-BuMgCl cannot be reviewed here.

[For reactn. of $\bar{C}$ with Et_2Zn and numerous homologs see (102).]

Ⓓ *ter*-Butyl alcohol (*1:6140*): m.p. 25.6°, b.p. 82.5°. [From $\bar{C}$ by shaking with aq. for 24 hrs. at room temp. (6), or on refluxing with 2 vols. aq for 8 hrs. (72), neutralizing with Na_2CO_3, salting out the alcohol with NaCl, drying over anhyd. Na_2CO_3, and distilling.]

Ⓓ Trimethylacetic acid (pivalic acid) (1:0410): m.p. 35.5°, b.p. 163–164°. [From $\bar{C}$ by

conversion to *ter*-BuMgCl (see above) and reactn. of latter with dry CO_2 (yields based on C̄, 75% (92), 62% (93), 42.5% (17)) (94).]

Ⓓ **Trimethylacetic anilide (pivalanilide):** m.p. 132–133° u.c. (103), 132.5–133° (17). [From C̄ by conv. to *ter*-BuMgCl (see above) and reactn. of latter with phenyl isocyanate in dry ether (17) (103) (104).]

Ⓓ **Trimethylaceto-*p*-toluidide (pivalo-*p*-toluidide):** m.p. 119–120° u.c. (103). [From C̄ by conversion to *ter*-BuMgCl (see above) and reactn. of latter with *p*-tolyl isocyanate in dry ether (103).]

Ⓓ **Trimethylaceto-α-naphthalide (pivalo-α-naphthalide):** m.p. 146–147° u.c. (103) [From C̄ by conversion to *ter*-BuMgCl (see above) and reactn. of latter with α-naphthyl isocyanate in dry ether (103).]

—— ***ter*-Butyl mercuric chloride:** long ndls. from aq. acetone as directed (105), m.p. 122–123° dec. (105). [From *ter*-BuMgCl with $HgCl_2$ (105).]

—— ***S*-*ter*-Butylisothiourea picrate:** m.p. 160–161° (106). [From C̄ with thiourea on htg. in alc. followed by conversion of the resultant hydrochloride to picrate (106); note, however, that, because of the lability of the *ter*-butyl radical, reactions carried out in MeOH or EtOH may give the corresp. *S*-methylisothiourea picrate, m.p. 224°, or *S*-ethylisothiourea picrate, m.p. 188°, and this definitely occurs (107) starting with *ter*-butyl iodide.]

—— ***N*-(*ter*-Butyl)phthalimide:** unreported.

—— ***ter*-Butyl 2,4,6-triiodophenyl ether:** unreported.

—— ***ter*-Butyl α-naphthyl ether:** unreported.

—— ***ter*-Butyl β-naphthyl ether:** unreported.

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3:7065 ACETYL CHLORIDE (Ethanoyl chloride)

$CH_3—C=O$ (with Cl on the C) C_2H_3OCl Beil. II - 173; II_1-(79); II_2-(175)

B.P.			F.P.	
55°	at 760 mm.	(1)	−112.0° (6)	D_4^{25} = 1.0983 (5)
51–52°	at 761 mm.	(2)		1.0982 (11)
52°	at 737 mm.	(3)		
51–52°		(12)		$D_4^{20.8}$ = 1.1037 (12)
51–52°	at 720 mm.	(4)		
51.8°		(5)		D_4^{20} = 1.1044 (8)
51.0°	at 760 mm.	(6)		n_D^{25} = 1.3878 (5)
50.92°	at 746 mm.	(7)		
50.6°	at 756 mm.	(8)		$n_D^{20.8}$ = 1.38831 (12)
50.2°		(9)		
50.08–50.12°	at 741 mm.	(10)		n_D^{20} = 1.38976 (4)
50°	at 740 mm.	(13)		1.3887 (8)

Colorless mobile liq. with sharp and penetrating odor. — Note that ordinary samples of C̄ may (according to their method of preparation) contain more or less PCl_3 (b.p. 75.95° at 760 mm.), $POCl_3$ (b.p. 107.2° at 760 mm.), $SOCl_2$ (b.p. 78.8°), AcOH (b.p. 118.2°), Ac_2O (b.p. 140.0°), or various acetylated derivs. of phosphorous acid (if present in large amt. the last in part form a white ppt. on long stdg.), removal of which is difficult; the presence of these impurities doubtless accounts for various instances of abnormally high b.p.'s cf. (7). — C̄ may be freed from dissolved HCl and from AcOH by distn. with dimethylaniline (13) or by treatment with powdered basic oxides, hydroxides, carbonates, etc. (14).

PREPARATION OF C̄

C̄ can be prepared from various sources with a wide variety of reagents; examples of the more important types of combinations are given below grouped under indicated subheadings. — It must also be recognized that many other processes (notably for manufacture of Ac_2O) involve the formation of C̄ but immediately utilize it without separate isolation; these cannot be included here.

Preparation of C̄ from AcOH. [For prepn. of C̄ from AcOH with PCl_3 (79% yield (20)) (15) (16) (7) (17) under press. at 80° (yield 100% (18)) or in Ac_2O (85% yield (19)) see indic. refs. (note particularly the formn. of Ac_2O and of $AcO.P(OH)_2$ discussed in (17)): with $PCl_3 + ZnCl_2$ (90% yield) see (20); with PCl_5 (80% yield (20)) (21) see indic. refs.; with $POCl_3$ (22) (23) see indic. refs.; with P_2O_5 + HCl gas at 0° see (24) (25); with $P + Cl_2$ in $POCl_3$ see (26).]

[For prepn. of C̄ from AcOH with $SOCl_2$ (46% yield (20)), with $S_2Cl_2 + Cl_2$ at −4° in pres. of Fe (95.5% yield (27)), with $ClSO_3H$ (20–25% yield (28)); with sodium chlorosulfonate (29) in pres. of NaCl or $Na_2S_2O_7$ (30) (31), or with $SiCl_4$ in toluene (85% yield (32)), see indic. refs.]

[For prepn. of C̄ from AcOH with $COCl_2$ (3:5000) at 110–120° (33) in vapor phase at 160° over $MgCl_2$ on diatomaceous earth (34) cf. (35) (36); with an arylsulfochloride such as *p*-toluenesulfonyl chloride + NaCl (30); with another org. acid chloride such as chloroacetyl chloride (3:5235) (37), dichloroacetyl chloride (3:5290) (38), or benzoyl chloride (3:6240) (yield 85–88% (39), 70% (42)) (40) (41); with benzotrichloride (3:6540) (90% yield (42)) see indic. refs.]

Preparation of C̄ from salts of acetic acid. [For prepn. of C̄ from NaOAc (or other metallic acetates) with $POCl_3$ (43) (44); with SO_2Cl_2 (45) (46); with sodium chlorosulfonate

(29) cf. (30); with $SiCl_4$ (47) (48); with $COCl_2$ at 120° under press. (49); with p-toluenesulfonyl chloride (50); with benzoyl chloride (3:6240) (40) see indic. refs.; from NaOAc/H_2SO_3 compd. with Cl_2 see (51).]

Preparation of Č from acetic anhydride. [For prepn. of Č from Ac_2O (1:1015) with Cl_2 (52); with dry HCl gas at 100° (52) or in continuous process at 85–90° (93% yield (53)) or under 18–42 atm press. (100% yield (54)); with PCl_3 (15); with PCl_5 (21); with $SOCl_2$ at 20–25° (SO_2 being evolved) (55), or with sodium chlorosulfonate (29) see indic. refs.]

[For prepn of Č from Ac_2O (1:1015) with phosgene (3:5000) + cat. (56); with benzoyl chloride (3:6240) (77% yield (42)) (41) (40); with oxalyl (di)chloride (3:5060) (80–95% yield (57)); with benzo-trichloride (3:6540) + $ZnCl_2$ (33% yield (58)); with benzyl chloride (3.8535) + cat. (59) see indic. refs.; for formn. of Č as by-prod. from reactn. of ethylene with Cl_2 in Ac_2O see (60).]

Preparation of Č from methyl chloride. [For prepn. of Č from CH_3Cl (3:7005) with CO at 700–800° over pumice contg. sodium metaphosphate (61) or with CO, $COCl_2$, or COS at 700–900° in pres. of metallic cat. (62) see indic. refs.]

Preparation of Č from miscellaneous sources. [For prepn. of Č from 1,1,1-trichloroethane (methylchloroform) (3:5085) by partial cat. hydrolysis (63) (64); from ketene + liq. HCl (65) or with HCl gas over activated carbon at 100° (100% yield (66)); from ethyl, isobutyl, isoamyl, benzyl, phenyl, or p-tolyl acetates with $SiCl_4$ (67); from α-chloroethyl acetate (3:7625) (68) (69) or α,β-dichloroethyl acetate (69) with $ZnCl_2$ (68) or over pumice at 250–300° (69); from β-bromo-α,β-dichlorovinyl ethyl ether with AcOH (70); from acetyl bromide with HCl gas at ord. temp. (71); from N,N-diacetylaniline (diacetanilide) with HCl gas at 150–170° (72); from diacetyl sulfite (see below) with $SOCl_2$ (73) see indic. refs.]

PYROLYSIS OF Č

[Č in absence of cat. is stable to heat up to at least 450° (74). — Č passed at 700–850° over hot Pt wire gives ethylene + CO + HCl (75), but at 400° over Pt on pumice gives (74) 45% MeCl (3:7005) + 49% CO + 5% H_2. — Č over Cu filings at 350° is partially decomposed yielding (74) MeCl (3:7005) + CO + CO_2 + H_2 + dehydroacetic acid (1:0700) + acetone. — Č over $ZnCl_2$ on pumice at 400° gives (74) HCl + dehydroacetic acid (1:0700) + gas mixt contg. 87% CO_2 + 4% CO + 2% H_2. — Č over Ni at 420° gives (76) HCl + gas mixt. contg. 62% CO + 32% H_2. — For studies on pyrolysis of Č over Al_2O_3, Cu_2Cl_2, CuO, Ni, etc., see (74).]

REACTIONS OF Č WITH INORGANIC REAGENTS

Reaction of Č with H_2O (hydrolysis). Č reacts violently with aq. hydrolyzing to AcOH (1:1010) + HCl (for kinetic studies see (77)); for use of this reactn. in volumetric detn. of H_2O in org. liquids see (185) (78). — Because of its ease of reactn. with aq. Č is widely used for condensations, ring closures, etc.

Reaction of Č with NH_3 and similar cpds. Č with cold conc. aq. NH_4OH (16) or Č with liq. NH_3 (79) gives (yields: 77% (16), 88% (79)) acetamide, very sol. aq., m.p. 81.5°, b.p. 222° (best recrystd. from dry AcOEt by addn. of dry ether).

[The direct reaction of Č with NH_2OH (or its salts) seems to be unreported, but the presumable prod., viz., N-acetylhydroxylamine (acethydroxamic acid) [Beil. II-187, II_1-(85), II_2-(181)], very eas. sol. aq. or alc., insol. ether, cryst. from EtOAc, m.p. anhydrous 89°, contg. crystal aq. 57°, has been obtd. indirectly.]

[The direct reactn. of Č with hydrazine hydrate, $NH_2.NH_2.H_2O$, seems to be unreported, but the presumable prod., viz., acethydrazide (acetylhydrazine) [Beil. II-191, II_1-(86), II_2-(185)], ndls. from alc., m.p. 67°, has been obtd. by indirect means.]

Reaction of $\bar{C}$ with halogens. [$\bar{C}$ with Cl_2 in CCl_4 in light (80) or in pres. of I_2 (82) gives mainly chloroacetyl chloride (3:5235); for study of mechanism of chlorination see (81); for influence of $\bar{C}$ on chlorination of AcOH or Ac_2O see (82), on bromination of AcOH see (83).]

[For studies of $\bar{C}$ with Br_2 see (84) (85) (86).]

Reaction of $\bar{C}$ with inorganic acids. [$\bar{C}$ with dry HBr gas for 2 hrs. gives (80% yield (87)) acetyl bromide [Beil. II-174, II_1-(79), II_2-(176)], b.p. 76.7° at 760 mm., $D_4^{15.8}$ = 1.6625, $n_D^{15.8}$ = 1.45370; for details on this equilibrium see (88).]

[$\bar{C}$ with 3 pts. dry HI in the cold gives (70% yield (87)) (89) acetyl iodide [Beil. II-174, II_1-(80), II_2-(177)], b.p. 104–106° at 735 mm. (89) (for studies of use of AcI in splitting of aliphatic ethers (90) or in addn. to unsatd. hydrocarbons (91) see indic. refs.).]

[$\bar{C}$ with cold conc. H_2SO_4 (1 mole) forms a mol. cpd. (88) (92) which can even be obtd. in cryst. form (92); this cpd. loses HCl only upon htg. (88) (92), and the residual acetyl hydrogen sulfate [Beil. II-170, II_1-(78), II_2-(174)] which might be expected is transformed into sulfoacetic acid and other prods. (92). — $\bar{C}$ with nitrosylsulfuric acid in CCl_4 evolves NOCl and yields acetyl HSO_4 which rapidly changes to sulfoacetic acid (93)]

[$\bar{C}$ with $ClSO_3H$ stood for several days (94) (95) evolves HCl and forms the transient acetyl sulfonyl chloride, $CH_3.CO.O.SO_2Cl$; above 45° this intermediate rearr. to sulfoacetyl chloride which with water hydrolyzes to sulfoacetic acid; $\bar{C}$ with $ClCO_3H$ at 60–140°, however, *also* undergoes condensation involving 4 moles of $\bar{C}$ with evoln. of HCl and formn. of an acid chloride which on hydrolysis with aq. gives (3% yield (94)) a monobasic acid of compn. $C_8H_8O_4$ [Beil. XVIII-412], m.p. 99°, which is either 2,6-dimethylpyrone-4-carboxylic acid-3 or 2-methylpyrone-1,4-acetic acid-6 (96); note that this acid is isomeric with but distinct from dehydroacetic acid (1:0700), m.p. 109°. — Note also that $\bar{C}$ in AcOH boiled with conc. H_2SO_4 gives (97) traces of 2,6-dimethylpyrone.]

[$\bar{C}$ with solid H_2O_2 (0.6 mole) yields (98) about 60% acetyl hydrogen peroxide (peracetic acid) [Beil. II-169, II_1-(78), II_2-(174)] accompanied by some diacetyl peroxide [Beil. II-170, II_1-(78), II_2-(174)]. — $\bar{C}$ with liq. H_2S yields (99) "dithioacetic acid anhydride," $(CH_3.CS)_2S$, white cryst., m.p. 225° (99); note that, although neither $\bar{C}$ nor Ac_2O separately treated with H_2S gas shows any appreciable reaction, yet Ac_2O contg. 2% $\bar{C}$ absorbs H_2S giving (70% yield (100)) thiolacetic acid [Beil. II-230, II_1-(101), II_2-(208)], $CH_3.CO.SH$, b.p. 93°. — $\bar{C}$ (4 moles) with H_2S_3 + $ZnCl_2$ yields (101) diacetyl trisulfide.]

Reaction of $\bar{C}$ with salts of inorganic acids. [$\bar{C}$ with metal oxides in $CHCl_3$ at −60 to −20° yields (102) the corresp. metallic chlorides. — $\bar{C}$ with Sb_2S_3 at 300–350° (103) or with K_2S (104) gives diacetyl sulfide [Beil. II-232], b.p. 120°. — $\bar{C}$ with $PbSO_3$ gives (72) diacetyl sulfite which with $SOCl_2$ gives $\bar{C}$ + SO_2 (72).

[$\bar{C}$ (6 pts.) with KNO_3 (first fused, then powdered) (1 pt.) (105) or $\bar{C}$ with $Pb(NO_3)_2$ (106) gives mainly (yields: 81–85% (105), 58% (106)) acetic anhydride (1:1015).]

[$\bar{C}$ with NaN_3 in di-isoamyl ether stood overnight (108) (109), then warmed at 60–70°, evolves N_2 and gives (86% yield (107)) methyl isocyanate [Beil. IV-77, IV_1-(337), IV_2-(578)], b.p. 27.4–27.8°; note, however, that $\bar{C}$ with NaN_3 in AcOH evolves N_2 and gives (50–63% yield (110)) *N*-methylacetamide, m.p. 27–28°, b.p. 202–204° (presumably by cleavage of the CH_3NCO and acetylation of the $MeNH_2$).]

[$\bar{C}$ with $NaHF_2$ in Ac_2O (111), with KF in AcOH (41) (42), AgF (112), ZnF_2 (112) (113), HgF_2 (114), C_6H_5HgF (115), SbF_3 (112) (116), or AsF_3 (112) gives (yields: 132% on $\bar{C}$ or 66% on $NaHF_2$ (111), 76% (41) (42), 40% (113), 30.8% (116)) acetyl fluoride, b.p. 20.8° at 770 mm.]

[$\bar{C}$ with $AlCl_3$ in CS_2 at −10° gives (117) a mol. cpd., $\bar{C}.AlCl_3$, as a pale yel. gummy mass; $\bar{C}$ with $AlCl_3.Et_2O$ gives EtOAc (70% yield (118)) + EtCl (3:7015) + $AlCl_3$. — $\bar{C}$ (1 mole) with $AlCl_3$ (6 moles) in $CHCl_3$ gives (124) $(CH_3CO)_2.CH.CCl_2.O.AlCl_2$ (125) which with

aq. yields (124) (125) acetylacetone (1:1700). — Note also that $\bar{C}$ forms other analogous complexes. e.g., $\bar{C}.BCl_3$ (119), $\bar{C}.BF_3$ (119), $\bar{C}.SbCl_5$ (119) (for use of these in splitting of ethers see (119)).]

[$\bar{C}$ with 2 pts. sublimed $FeCl_3$ in CS_2 for 24 hrs. gives (small yield (120)) dehydroacetic acid (1:0700).]

[$\bar{C}$ with CaI_2 in s.t. at 70–75° for 120 hrs. gives (121) acetyl iodide (see above under HI).]

Reaction of $\bar{C}$ with esters of inorganic acids. [$\bar{C}$ with Me_2SO_4 (1 mole) + trace of $ZnCl_2$ at 140–150° evolves HCl and gives (20–25% yield (122)) dimethyl sulfoacetate, b.p. 155–165° at 20–22 mm. (122). — $\bar{C}$ + di-*n*-propyl sulfite + trace $ZnCl_2$ at 170–200° gives (80% yield (123)) *n*-propyl acetate (1:3075).]

Reaction of $\bar{C}$ with metals. [$\bar{C}$ in excess with metallic Zn gives a solid of compn. $C_{16}H_{18}O_4$ (126), now (127) thought to be 3,8-diacetyl-5,6-dimethyldecatetraene-3,4,6,7-dione-2,9. — $\bar{C}$ with metallic Zn in dry ether yields (128) EtOAc (1:3015) and AcOH (1:1010). — $\bar{C}$ with metallic Zn in dry dioxane (1:6400) gives (85% yield (128)) (129) ethylene glycol diacetate (1:3511). — $\bar{C}$ with CuH evolves H_2 and gives (130) cf. (131) EtOAc (1.3015) + ethylidene diacetate (1·3383).]

REACTIONS OF $\bar{C}$ WITH ORGANIC REAGENTS

Reactions of $\bar{C}$ with Hydrocarbons

Reactions of $\bar{C}$ with alkanes. [$\bar{C}$ with *n*-butane (or isobutane) + $AlCl_3$ at 60° for 15 hrs. under press. gives (small yield (132)) isobutyl methyl ketone (1 5430) — $\bar{C}$ with *n*-pentane + $AlCl_3$ at 15° at ord. press. gives (10% yield (133)) (134) 2,3-dimethylpentanone-4 (*unsym.*-isopropyl-methyl-acetone) [Beil. I-703, I_1-(360)], b p. 135–136° (oxime, b.p. 101–105° at 20 mm., semicarbazone, m.p. 114° (133)) accompanied (134) by some 2,3-dimethylpenten-3-one-2 (*unsym.*-isopropylidene-methyl-acetone) [Beil. I_2-(796)] (corresp. semicarbazone, m.p. 192.5° (134)). — $\bar{C}$ with *n*-hexane + $AlCl_3$ in similar fashion gives (7% yield (135)) (134) 3-ethyl-2-methylpentanone-4 (*unsym* -ethyl-isopropyl-acetone) [Beil. I-707], b.p. 154–155° (semicarbazone, m.p. 120° (135)) accompanied by a little 3-ethyl-2-methylpenten-2-one-4 (*unsym.*-ethyl-isopropylidene-acetone), b p. 177–178° (semicarbazone, m p. 220° (135).]

Reactions of $\bar{C}$ with alkenes. [$\bar{C}$ in the pres of suitable cat. can add to olefin linkages forming halogenated ketones: e g , $\bar{C}$ with ethylene + $AlCl_3$ at 0° (137) (138) or $\bar{C}$ + ethylene over activated carbon at 100° and 50 atm. (139) gives (yields· 53% (136), 33% (137)) (138) cf. (60) β-chloroethyl methyl ketone (3:7640) (note that $\bar{C}$ + ethylene + $AlCl_3$ in CS_2, latter subsequently replaced by C_6H_6, goes further yielding (140) benzylacetone [Beil VII-314, VII_1-(167)], b.p. 235°). — For studies of analogous cat. addn. of $\bar{C}$ to 2-methylbutene-2, 2,3-dimethylbutene-2, and 2-methylhexene-2 see (141).]

Reactions of $\bar{C}$ with alkynes. [$\bar{C}$ in the pres. of suitable cat. can also add to a triple unsatd linkage yielding olefinic chloroketones: e.g., $\bar{C}$ with acetylene + $AlCl_3$ at 15° (142) (143) or other cat. (143) gives (25% yield (142)) β-chlorovinyl methyl ketone, b.p. 35–38° at 12 mm. (143). — $\bar{C}$ with butyne-1 (ethylacetylene) + $SnCl_4$ gives (144) 4-chlorohexen-3-one-2, b p 46–53° at 10 mm., $D_4^{25} = 1.0973$, $n_D^{25} = 1.4906$ (144); for analogous reactions with pentyne-1, hexyne-1, hexyne-3, heptyne-1, octyne-4, decyne-5, and dodecyne-6 together with corresp constants of prods. see (144)]

Reaction of $\bar{C}$ with cycloparaffins (cycloalkanes). [$\bar{C}$ in the pres of $AlCl_3$ also condenses with cycloalkanes eliminating HCl; e g., $\bar{C}$ (1.9 moles) + cyclopentane (1:8400) (5 4 moles) + $AlCl_3$ (2.2 moles) at 0° gives (145) cyclopentyl methyl ketone (acetylcyclopentane), b.p. 159.5–160 5° at 760 mm., $D_{20}^{20} = 0.9172$, $n_D^{20} = 1.44351$ (145) (semicarbazone, m.p. 142–143° (145)); $\bar{C}$ + methylcyclopentane (1:8403) + $AlCl_3$ similarly gives (145) 1-

methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane) accompanied by some 1-methylcyclopenten-1-yl-2 methyl ketone (1-acetyl-2-methylcyclopentene-1) (see below).]

[C̄ *in the pres. of $AlCl_3$ also condenses with cyclohexane, but here the reaction involves* in addn. a change from a 6-membered to 5-membered ring: e.g., C̄ with cyclohexane (1:8405) + $AlCl_3$ gives (135) (146) (147) (148) 1-methylcyclopentyl-2 methyl ketone (1-acetyl-2-methylcyclopentane), b.p. 167–168° at 759 mm., $D_4^{20} = 0.8976$, $n_D^{20} = 1.4404$ (semicarbazone, m.p. 162.5–163° (148), 158° (146); *p*-nitrophenylhydrazone, m.p. 102.5° (148)), accompanied under certain circumstances (135) by *1-methylcyclopenten-1-yl-2 methyl* ketone (1-acetyl-2-methylcyclopentene-1), b.p. 185–187° (135) (oxime, m.p. 85–85.5° (148), *p*-nitrophenylhydrazone, m.p. 162° (148), semicarbazone, m.p. 221° (148), 220° (135)); note that various hydrocarbon by-products are also formed. — C̄ + methylcyclohexane (hexahydrotoluene) (1:8410) + $AlCl_3$ at room temp. *similarly* gives (149) *1-acetyl-2,3-dimethylcyclopentane*, b.p. 182–184° at 754 mm., $D_{20}^{20} = 0.8969$, $n_D^{22} = 1.44551$ (semicarbazone, m.p. 152°) (149).]

Reaction of C̄ with cycloalkenes. [C̄ in the pres. of suitable cat. *adds* to unsatd. linkages of cycloalkenes: e.g., C̄ with cyclopentene (1:8037) + $AlCl_3$ (2 moles) in cyclohexane at −15° gives (50% *yield* (150)) *cyclopentyl methyl ketone* (*1-acetylcyclopentane*) (for constants see above under C̄ + cyclopentane); note, however, that C̄ + cyclopentene (1:8037) + $AlCl_3$ at −14° in CS_2 (the latter being subsequently replaced by benzene) gives (140) 1-acetyl-3-phenylcyclopentane (note rearr.).]

[C̄ with cyclohexene (1:8070) + $AlCl_3$ (2 moles) in cyclohexane gives (53% yield (150)) cyclohexyl methyl ketone (1-acetylcyclohexane) [Beil. VII-22, VII_1-(16)]. — C̄ with cyclohexene (1:8070) + $AlCl_3$ (1 mole) in CS_2 gives (21% yield (151)) (152) cyclohexen-1-yl-1 methyl ketone (1-acetylcyclohexene-1) (tetrahydroacetophenone) [Beil. VII-58, VII_1-(49)], b.p. 201–202°, $D_4^{20} = 0.9655$, $n_D^{20} = 1.4881$ (oxime, m.p. 99°, semicarbazone, m.p. 220–221°). — C̄ *with cyclohexene* (1:8070) + $AlCl_3$ *in* CS_2 *at* −15° *gives* by addn. a prod. supposed (153) to be 2-chlorocyclohexyl-1 methyl ketone (since it can be converted by loss of HCl to tetrahydroacetophenone (above)) but which when reacted with C_6H_6 + $AlCl_3$ gives (140) 4-phenylcyclohexyl-1 methyl ketone (1-acetyl-4-phenylcyclohexane); in just which *phase rearr. occurs has not been established with certainty.*]

Reaction of C̄ with aromatic hydrocarbons. C̄ with aromatic hydrocarbons in the presence of various cat. (notably $AlCl_3$) evolves HCl and yields aryl methyl ketones; examples are cited in the following paragraphs.

[C̄ with C_6H_6 + $AlCl_3$ (154) in CS_2 (155) gives (70% yield (155)) methyl phenyl ketone (acetophenone) (1:5515) accompanied by a little 1,3-diphenylbuten-2-one-1 (dypnone) cf. (155); for study of relative reactivity in this sense of AcF, AcCl, AcBr, and AcI see (111); for study of influence of other cat., e.g., $FeCl_3$ (156) (157), $TlCl_3$ (158), $ZrCl_4$ (159), UCl_4 (160), $BeCl_2$ (161), Al powder (162) or Cr powder (163), or for study of effect of various solvents with $AlCl_3$ (164) see indic. refs.]

[C̄ with toluene + $AlCl_3$ gives (70% yield (165)) (166) methyl *p*-tolyl ketone (1:5530); for study of use of $BeCl_2$ (80% yield (161)) or of 39 other metallic chlorides (167) (168) see indic. refs. — For reactn. of C̄ + $AlCl_3$ with a long series of homologous monoalkylbenzenes see (169) (170), with *p*-cymene (1:7505) see (171); many other, similar cases cannot be included here.]

[C̄ with naphthalene (1:7200) + $AlCl_3$ in CS_2 gives a mixt. (75% yield (172)) comprising 50–60% 1-acetylnaphthalene (1:5600) + 15–20% 2-acetylnaphthalene (1:5153). — C̄ with 1-methylnaphthalene (1:7600) + $AlCl_3$ in nitrobenzene at −3° gives (173) cf. (174) 1-aceto-4-methylnaphthalene; C̄ with 2-methylnaphthalene (1:7605) + $AlCl_3$ in nitrobenzene gives a mixt. (64% yield (175)) comprising mainly 6-acetyl-2-methylnaphthalene accompanied by some 8-acetyl-2-methylnaphthalene.]

[$\bar{C}$ with biphenyl (1:7175) + $AlCl_3$ in CS_2 (176) or C_6H_6 (177) gives (yields: 90% (176), 70% (177)) 4-acetylbiphenyl (*p*-phenylacetophenone) (1:5201); under appropriate conditions $\bar{C}$ with biphenyl + $AlCl_3$ in CS_2 gives (yields: 45% (176), 43% (178)) 4,4′-diacetylbiphenyl.]

[$\bar{C}$ with acenaphthene (1:7225) + $AlCl_3$ in nitrobenzene (179) or with liq. HF (180) gives (29% yield (180)) 1-acetoacenaphthene.]

[Friedel-Crafts condensation can also be carried out with $\bar{C}$ and heterocyclic systems: e.g., $\bar{C}$ with thiophene + $SnCl_4$ in C_6H_6 gives (79–83% yield (181)) 2-acetylthiophene (methyl 2-thienyl ketone), $\bar{C}$ with thionaphthene + $AlCl_3$ in CS_2 gives (30% yield (182)) 3-acetylthionaphthene.]

Reactions of $\bar{C}$ with Organic OH (or SH) Compounds (or Their Metallic Derivatives)

Reactions of $\bar{C}$ with alcohols. [$\bar{C}$ reacts with alcs. in general yielding the corresp. acetates: e g., $\bar{C}$ with MeOH (1:6120) yields methyl acetate (1:3005), $\bar{C}$ with EtOH (1:6130) yields EtOAc (1:3015), etc ; for studies on rate of reactn. of $\bar{C}$ with EtOH in ether (1), or with β-chloroethyl alc. in dioxane (182) (183), or with benzyl alc. or cyclohexanol (182) see indic. refs.] — For use of $\bar{C}$ in quant. detn. of OH groups in prim. and sec. alcs. see (186) (187) (188) cf. (185).

[Special interest, however, attaches to reaction of $\bar{C}$ with *ter*-alcohols: under ord. conditions these react with $\bar{C}$ to exchange Cl for OH yielding alkyl chloride + AcOH (e.g., $\bar{C}$ + *ter*-butyl alc. giving *ter*-BuCl + AcOH); note, therefore, that under special conditions $\bar{C}$ with *ter*-alcs. also gives the corresp. esters; e g , $\bar{C}$ with *ter*-butyl alc. (1:6140) in dry ether + Mg (189) (190) or dimethylaniline (191) or in xylene with pyridine (192) gives (yields: 98% (192), 83% (189), 63–68% (191), 45–55% (190)) *ter*-butyl acetate (1:3057); other *ter*-alcs. (189) and other acid chlorides (191) behave similarly.]

[For reactn. of $\bar{C}$ with cellulose (or cotton) see (193) (194) (195); with polyoxymethylenes see (196).]

[$\bar{C}$ with mercaptans yields the corresp. thiolacetates: e g., $\bar{C}$ with C_2H_5SH gives (80% yield (197)) ethyl thiolacetate, $CH_3CO.S\ C_2H_5$, b.p. 116–117°, $D_4^{25} = 0.9755$, $n_D^{23} = 1.4503$ (197).]

Reactions of $\bar{C}$ with phenols. $\bar{C}$ can react with phenols in either or both of two modes: on one hand it can acetylate the phenolic OH yielding the corresp. phenol acetates, or in the pres. of suitable cat. or solvents it can condense with one or more of the nuclear H atoms yielding phenolic ketones. Furthermore the phenol acetates can more or less readily be caused to rearr. into phenolic ketones (Fries rearr.) so that the chemistry of the two classes is closely related and so voluminous that it cannot be given extensive discussion here.

[$\bar{C}$ with phenol (1:1420) directly (198) (199) or in C_6H_6 + Mg (200) gives (yields: 92% (200), 90% (199)) phenyl acetate (1:3571); other mono-, di-, and polyhydric phenols behave analogously.]

[$\bar{C}$ with phenol (1:1420) + $FeCl_3$ in CS_2 (156) (201) or phenyl acetate (above) + $AlCl_3$ in nitrobenzene at 20–25° for 24 hrs. (202) gives (yields: 75% (202), 33% (201)) *p*-hydroxyacetophenone (1.1527), m.p. 109° (for extensive review of the Fries rearr. reactn. see (203)); the corresp. analogous reactns. of $\bar{C}$ with other mono-, di-, and polyhydric phenols are legion and will not be cited here.]

[For study of series of mol. cpds. of $\bar{C}$ with various benzeneazophenols see (230).]

Reaction of $\bar{C}$ with phenol ethers. With phenol ethers where no phenolic OH remains to interfere $\bar{C}$ reacts in the pres. of suitable cat. in the Friedel-Crafts sense: e g. [$\bar{C}$ (2 moles) with methyl phenyl ether (anisole) (1:7445) (1 mole) + $AlCl_3$ (2 moles) gives (75% yield

(204)) (205) *p*-methoxyacetophenone (*p*-acetylanisole) (1:5140); note that C̃ + anisole do not react in the pres. of AlF_3 or ZnF_2 (111). — Countless analogous condensations of C̃ with other phenol ethers cannot be discussed here].

Reaction of C̃ with enols (or their metallic derivatives). [The reaction of C̃ with ethyl acetoacetate (1:1710) leads according to circumstances to either or both of two very closely similar derivatives; one of these is ethyl *O*-acetylacetoacetate (ethyl β-acetoxycrotonate) (*A*) [Beil. III-373, III_1-(135), III_2-(255)], b.p. 212–214° sl. dec. (206), D_4^{20} = 1.060 (207), n_D^{20} = 1.4447 (207); the other is ethyl α-acetylacetoacetate (ethyl diacetylacetate) (*B*) [Beil. III-751, III_1-(263), III_2-(467)], b.p. 209–211° (208), D_4^{20} = 1.093 (207), n_D^{20} = 1.4687 (207); note that the latter (*B*) as liquid is 100% enolized (209) (210) and this prop. is used (211) for detn. of both *A* + *B* in their mixtures. — Note furthermore that the *O*-ester (*A*) by suitable htg. (212) (213) (214) (215) (216) can be converted to the isomer (*B*).]

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Reaction of $\bar{C}$ with Various Organometallic Compounds

Reaction of $\bar{C}$ with Grignard reagents. [The normal reaction of $\bar{C}$ with 1 mole RMgX is to eliminate MgXCl and yield the corresp. ketone; e.g., $\bar{C}$ with EtMgBr in pres. of $CdCl_2$ gives (46% yield (250)) ethyl methyl ketone (1:5405); in the presence of excess RMgX, however (and sometimes without excess), the ketone may react further to yield the corresp. tertiary alcohol; e.g., $\bar{C}$ with C_6H_5MgBr gives 39% yield (251) diphenyl-methyl-carbinol; countless other examples cannot be included here.]

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(263) EtHgCl + butanone-2 (1:5405), but $\bar{C}$ with dibenzylmercury or with benzylmercuric chloride shows little reaction (262) even after refluxing 2 weeks.]

[$\bar{C}$ with tetraphenyltin in s.t. at 100° for 15 hrs. gives (very small yield (264)) of acetophenone (1:5515); for reactn. of $\bar{C}$ with tetraethyllead and use in detn. of latter in gasoline see (265).]

[$\bar{C}$ with triphenylbismuth in CCl_4 yields (266) acetophenone (1:5515).]

[$\bar{C}$ (2 moles) with $Ni(CO)_4$ (1 mole) in pet. ether gives (267) $4CO + NiCl_2$ + biacetyl the latter sepg. as a 1:1 addn. cpd. with the $NiCl_2$.]

Ⓓ Acetanilide: cryst. from hot aq., m.p. 114°. [From $\bar{C}$ with aniline (2 moles) followed by recrystallization to remove aniline hydrochloride. Note that even with aniline + aq. at room temp. acetanilide formn. occurs to extent of 35–45% but its proportion diminishes with increase of temp. (268).]

Ⓓ Acet-*p*-toluidide: cryst. from hot aq. or dil. alc., m.p. 153°. [From $\bar{C}$ + *p*-toluidine (2 moles) followed by recrystallization to remove *p*-toluidine hydrochloride.]

Ⓓ Acet-α-naphthalide: m.p. 159°.

Ⓓ Acet-β-naphthalide: m.p. 132°.

—— β-Acetophenylhydrazide (β-acetylphenylhydrazine) ($C_6H_5.NH.NH.COCH_3$) [Beil. XV-241, XV_1-(63)]: m.p. 128–129°. [Note that α-acetphenylhydrazide [Beil. XV-236, XV_1-(62)], m.p. 124°, is obtd. from α,β-diacetylphenylhydrazine [Beil. XV-245, XV_1-(64)], m.p. 107–108°, by partial hydrolysis.]

—— β-Acet-*p*-nitrophenylhydrazide [Beil. XV-478]: yel. ndls. from alc., m.p. 205–206°.

—— β-Acet-2,4-dinitrophenylhydrazide [Beil. XV-492]: yel. pr. from alc., m.p. 201° (269).

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3:7070 1-CHLOROBUTEN-3-YNE-1 C_4H_3Cl Beil. S.N. 13

(1-Chloro-2-vinylacetylene) $CH_2{=}CH{-}C{\equiv}C{-}Cl$

B.P.

55–57° at 760 mm. (1) (2) (3) (4) D_4^{20} = **1.0032** (1) (2) n_D^{20} = **1.4663** (1) (2)

1.0034 (4)

D_7^7 = **1.021** (4) n_D^7 = **1.4698** (4)

Colorless oil, not explosive when pure (3) (4). — $\bar{C}$ rapidly polymerizes on stdg. into black brittle solid sensitive to heat and shock (1); polymerization of $\bar{C}$ catalyzed by u.v. light, peroxide, ozonides, etc. (2). After addn. of hydroquinone (3) $\bar{C}$ can be distd. at ord. press.

[For prepn. of $\bar{C}$ from vinylacetylene by actn. of alkaline alk. hypochlorite solns. at 0° (yield 60–65% (4), 10% (1)) see (1) (2) (3) (4).]

C̄ treated as directed at −10° with conc. HCl + CuCl + NH_4Cl gives (56% yield (4)) 1,2-dichlorobutadiene-1,3 (3:9057) q.v.

C̄ with $NH_4OH/AgNO_3$ gives a white ppt.; with Ilosway reagt. a yel. ppt. (4).

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3:7075 2-CHLOROBUTENE-1

$CH_3.CH_2.C(Cl)=CH_2$ C_4H_7Cl Beil. I-204, I_1—, I_2—

B.P.		
58.4–58.6° at 760 mm. (1)	$D_4^{21} = 0.8950$ (2)	$n_D^{21} = 1.4115$ (2)
57–59° at 748 mm. (2)	$D_4^{15} = 0.9107$ (1)	$n_D^{14.1} = 1.4166$ (1)

C̄ forms with abs. EtOH an azeotrope, b.p. 53.6–54.0° at 760 mm., $D_4^{15} = 0.8945$, contg. 88.5% by wt. of C̄ (1).

[For formn. from *d,l*-1,2-dichlorobutane (3:7680) + alc. KOH (together with *cis*-(3:7110) and *trans* (3:7110) stereoisomers of 1-chloro-butene-1) see (1).]

3:7075 (1) Navez, *Bull. soc. chim. Belg.* **39**, 435–443 (1930). (2) Kroeger, Sowa, Nieuwland, *J. Org. Chem.* **1**, 167 (1936).

3:7080 2-CHLOROBUTADIENE-1,3 (Chloroprene)

$H_2C=CH-C(Cl)=CH_2$ C_4H_5Cl Beil. S.N. 12

B.P.		
59.4° at 760 mm. (1)	$D_4^{20} = 0.9585$ (2)	$n_D^{20} = 1.4583$ (1)
46.9° at 500 mm. (1)		1.4570 (31)
40.5° at 400 mm. (1)	$D_{20}^{20} = 0.9583$ (1)	1.4165 (2)
32.8° at 300 mm. (1)	0.9575 (31)	
6.4° at 100 mm. (1)		

Colorless liq. with ethereal odor suggesting C_2H_5Br. Only slightly sol. aq. but miscible with most org. solvs.

C̄ was first reported in 1931 (1) and given the name chloroprene (1) because of its analogy to 2-methylbutadiene-1,3 (isoprene) in structure and reactions. Despite its immense practical importance in the manufacture of various types of synthetic rubbers and plastics, comparatively little information on C̄ itself has been released for publication in the scientific literature.

[For a study of the toxicity and pathology of C̄ see (3); for study of poisoning by C̄ and its treatment see (4).]

[For studies of detn. of C̄ (5) by diazometric methods (6) (7) see indic. refs.]

PREPARATION OF C̄

C̄ has been prepared from vinylacetylene by addn. of HCl, from dichlorobutenes by elimination of 1 HCl, and from various other sources. Comparatively little on these methods has appeared in the scientific literature, and most of the information is available only through patents. Such of the latter as are here cited must be regarded only as illustrative as no guarantee of complete patent coverage can be offered.

From vinylacetylene. $\bar{C}$ is formed from vinylacetylene (8) by addn. of HCl from aqueous soln. in pres. of catalysts (usually copper salts). The initial step comprises 1,4 addition, and the primary product is 4-chlorobutadiene-1,2 (isochloroprene) (3:7225). Under certain conditions this may be isolated as the major reaction product, but it readily isomerizes (especially in the presence of cuprous chloride and/or other salts (9)) yielding chloroprene. When sufficient amounts of HCl are present further addition to $\bar{C}$ may also occur leading to 2,4-dichlorobutene-2 (3:5550) (see also below).

[For prepn. of $\bar{C}$ from vinylacetylene (8) with conc. aq HCl in pres. of Cu_2Cl_2 + NH_4Cl at 30° for 4 hrs. (65% yield) see (1) (47); for studies of this process in foreign laboratories see (10) (11) (12) (2) (24) For examples of patents on this process see (13)-(23) incl. For analogous prepn of certain homologs of $\bar{C}$ such as 2-chloro-3-methylbutadiene-1,3 (3:7290) and 2-chloro-3,4-dimethylbutadiene-1,3, etc., see (25) cf. (26).]

From dichlorobutenes. [For prepn of $\bar{C}$ from 3,4-dichlorobutene-1 (1,2-dichlorobutene-3) (3:5350) with powdered KOH or alc. NaOH see (27) (28), for 2,3-dichlorobutene-1 (3:9074) by thermal dehydrochlorination at 530° without cat. see (29); from 2,4-dichlorobutene-2 (3:5550) by dehydrochlorination (and isomerization) in pres. of fused KOH at 180–190° (30) or over silica gel or clay at 245–275° (31) cf. (30) see indic refs.; from 1,2-dichlorobutenes by dehydrochlorination with inorg. or org. bases in pres. of org. solvs. see (32)]

From other sources. [For prepn of $\bar{C}$ from 2,2,3-trichlorobutane (3:5680) by thermal dehydrochlorination over $MgCl_2/MgSO_4$ cat. see (33); from polychlorobutanes of 55–66% chlorine content (corresp. to dichloro-and trichlorobutanes) by thermal dehydrochlorination at 400–500° see (34) (note that 1-chlorobutadiene-1,3 (3.7210) is also formed; for separation of it from $\bar{C}$ see (35)): for formn of $\bar{C}$ from vinyl chloride (3:7010) with acetylene in pres. of aq. Cu_2Cl_2/NH_4Cl see (36).]

CHEMICAL BEHAVIOR OF $\bar{C}$

Addition Reactions

With chlorine. [$\bar{C}$ (2 moles) with Cl_2 (1 mole) in $CHCl_3$ at −10° in pres. of hydroquinone gives mainly (37) cf (38) (39) 1,2,4-trichlorobutene-2 (1,3,4-trichlorobutene-2) (3:9062) accompanied by other products such as 1,2,3-trichlorobutene-1 (37), b.p. 40–42° at 10 mm., $D_4^{15} = 1.3190$, $n_D^{15} = 1.4902$ (giving on oxdn. α,β-dichloropropionic acid); note: data also consistent with 2,3,4-trichlorobutene-1 (3:9064) and 1,2-dichlorobutadiene-1,3 (3:9057), b.p. 45–48° at 10 mm. (37), $D_4^{15} = 1.1905$ $n_D^{15} = 1.5065$ (37).]

With bromine. [$\bar{C}$ (0.3 mole) with Br_2 (0.25 mole) in $CHCl_3$ at 0–5° gives mainly (40) 2-chloro-1,4-dibromobutene-2, b p. 98–101° at 10 mm. (oxidizing with $KMnO_4$ to bromoacetic acid), accompanied by other products; note that in pres. of anti-oxidants distn. range of prod. is much wider perhaps owing to formn. of geom. stereoisomers.]

With iodine chloride. [$\bar{C}$ with ICl in $CHCl_3$ at −5° to 0° gives (70% yield (41)) a prod. regarded as 2,4-dichloro-1-iodobutene-2.]

With hydrogen chloride. [$\bar{C}$ with conc. aq HCl in pres. of Cu_2Cl_2 (42) adds HCl giving 2,4-dichlorobutene-2 (3:5550); for behavior of $\bar{C}$ in liq HCl see (43).]

With hydrogen bromide. [$\bar{C}$ (0.96 mole) with dry HBr (0.88 mole) in AcOH at −5° gives (72% yield on Br_2 (44)) 2-chloro-4-bromobutene-2, b.p. 150–152°; $D_4^{20} = 1.5264$, $D_4^{15} = 1.5335$; $n_D^{20} = 1.5160$, $n_D^{15} = 1.5185$; note that this prod. with aq. $KMnO_4$ oxidizes to AcOH + bromoacetic acid and adds 1 mole Br_2 giving 2-chloro-2,3,4-tribromobutane, b.p. 104.5–106° at 10 mm., $D_4^{15} = 2.1907$.]

With hydrochlorous acid. [The behavior of $\bar{C}$ with HOCl appears not to have been reported; 1,4 addition to $\bar{C}$ might be expected to yield 1,2-dichlorobuten-2-ol-4 and/or 2,4-dichlorobuten-2-ol-1, but neither is reported from any source; an isomer, viz., 2,3-

dichlorobuten-1-ol-4, b.p. 72–73° at 10 mm., $D_4^{20} = 1.3108$, $D_4^{15} = 1.3243$, $n_D^{20} = 1.4956$, $n_D^{15} = 1.4978$, has been reported (45) by indirect means.]

With hypobromous acid. [$\bar{C}$ with HOBr (from *N*-bromoacetamide) gives mainly (45) (note 3,4 addition) 2-chloro-4-bromobuten-1-ol-3, b.p. 77.0–77.25° at 10 mm.; $D_4^{20} = 1.6710$, $D_4^{15} = 1.6770$; $n_D^{20} = 1.5228$, $n_D^{15} = 1.5249$; this prod. in $CHCl_3$ adds 1 mole Br_2 giving 3-chloro-1,3,4-tribromobutanol-2, m.p. 69.5–71°.]

With alkyl hypoiodite. [$\bar{C}$ with MeOI (from MeOH + HgO + I_2) gives (62% yield (46)) 2-chloro-4-iodo-3-methoxybuten-1, b.p. 76.5–77.0° at 10 mm., $D_4^{20} = 1.7135$, $D_4^{15} = 1.7209$; $n_D^{20} = 1.5312$, $n_D^{15} = 1.5338$. — $\bar{C}$ with EtOI (from EtOH + HgO + I_2) gives (46% yield (46)) 2-chloro-4-iodo-3-ethoxybuten-1, b.p. 82–83° at 10 mm.; $D_4^{20} = 1.6163$, $D_4^{15} = 1.6231$; $n_D^{20} = 1.5198$, $n_D^{15} = 1.5220$. — Note for both these cases the same type of 3,4 addn. observed for HOBr above.]

With sulfur dioxide. [$\bar{C}$ in ether contg. pyrogallol treated with SO_2 at 100–105° in s.t. for 12 hrs. gives in very small amt. (2.5% (47)) an addition prod. 3-chloro-1-thiacyclopenten-3 dioxide (chloroprene sulfone).]

With naphthoquinone-1,4. $\bar{C}$ (2 moles) with α-naphthoquinone (1:9040) (1 mole) in C_6H_6 refluxed 3 hrs. and the intermediate addition prod. suspended in alc. NaOH and oxidized with air gives (1) 2-chloroanthraquinone (3:4022).

With maleic anhydride. $\bar{C}$ (1+ moles) with maleic anhydride (1:0625) (1 mole) warmed at 50° then boiled with aq. gives (77% yield (1)) 4-chloro-1,2,3,6-tetrahydrophthalic acid, cryst. from aq., m.p. 173–175° cor. (1).

POLYMERIZATION OF $\bar{C}$

$\bar{C}$ readily polymerizes at 30–35° in light from a 150-watt lamp in 48–80 hours (26); for study of various types of polymers from $\bar{C}$ alone see (1). Furthermore, $\bar{C}$ with various other unsaturated compounds undergoes copolymerization processes. The practical importance of the polymers and copolymers thus obtained can scarcely be overestimated, but the field is so large, so interlocked, and so rapidly developing that any attempt to organize it is quite beyond the scope of this book. Attention is here directed, however, to a few scientific papers of interest in this connection.

[For studies on structure of polychloroprene see (48) (49); for study of polymers of $\bar{C}$ by ozonization and HNO_3 oxidn. see (50); for detn. of unsaturation in polymers of $\bar{C}$ see (51); for permeability of polychloroprene to gas see (52).]

[For study of influence of tetralin peroxide (53) in nitrobenzene (54) or of high-frequency field (55) (56) on polymerization of $\bar{C}$ see indic. refs.; for photopolymerization of $\bar{C}$ see (57); for study of kinetics of polymerization of $\bar{C}$ in di-*n*-butyl phthalate soln. in pres. of dibenzoyl peroxide see (58); for detection of free radicals in peroxide polymerization of $\bar{C}$ see (59).]

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... (*U.S.S.R.*)
... *Compt. rend*,
... ville, *Rubber*
... 1938). (58)
... *C.A.* **35**, 371
... –407 (1943);
C.A. **38**, 4903 (1944).

II-151, II_1-(70), II_2-(163)], b.p. 117–118° (3); for corresp. react. with Pb propionate or Na *n*-butyrate see (3).]

[$\bar{C}$ in C_6H_6 with $ZnCl_2$ + HCl gas at 55–65° gives (52) cf. (28) benzyl chloride (3:8535). — $\bar{C}$ with chlorobenzene (3:7903) + dehydrating agts. gives (28) *p*-chlorobenzyl chloride (3:0220). — $\bar{C}$ with toluene + $SnCl_4$ gives (35–40% yield (53)) *p*-methylbenzyl chloride (*p*-xylyl chloride) (3:8660) together with other prods.]

[$\bar{C}$ in AcOH soln. without cat. condenses with aromatic nuclei: e.g., $\bar{C}$ with toluene in AcOH gives (25% yield (15)) a mixt. of *o*-xylyl chloride (3:8710) and *p*-xylyl chloride (3:8660); for analogous reactns. of $\bar{C}$ in AcOH with *o*-xylene (1:7430), *m*-xylene (1:7420), pseudocumene (1:7470), mesitylene (1:7455), naphthalene (1:7200), tetralin (1:7550), anisole (1:7445), etc., see (15).]

[By virtue of its reactive halogen atom $\bar{C}$ reacts readily with Grignard reagents giving (54) the corresp. methyl ethers: e.g., $\bar{C}$ with *n*-BuMgBr gives (67% yield (55)) (56) *n*-amyl methyl ether (1:7905); $\bar{C}$ (2 moles) with decamethylene-*bis*-MgBr gives (53% yield (57)) dodecanediol-1,12-dimethyl ether; $\bar{C}$ with $CH_3—C{\equiv}C—MgBr$ gives (58) $CH_3.C{\equiv}C.CH_2OCH_3$; $\bar{C}$ with $Br—Mg.C{\equiv}C—MgBr$ gives (63% yield (32)) 1,4-dimethoxybutyne-2; $\bar{C}$ with C_6H_5MgBr gives (60% yield based on initial C_6H_5Br (59)) benzyl methyl ether (1:7475); $\bar{C}$ with benzyl MgCl gives mainly (60) cf. (61) (62) methyl β-phenylethyl ether (ω-methoxyethylbenzene) [Beil. VI-479, VI_1-(238)], b.p. 185–187° (61), accompanied by some *o*-tolylcarbinol methyl ether and *p*-tolylcarbinol methyl ether, cf. (60).]

[In the pres. of appropriate catalysts $\bar{C}$ adds to olefinic unsatd. linkages, addition occurring as if $\bar{C}$ dissociated into (Cl-) and ($CH_3O.CH_2$-) radicals; examples of these addition reactions are given as follows: $\bar{C}$ with ethylene + $BiCl_3$ at 80° under 700–800 lbs. press. for 7 hrs. gives (63) *γ-chloro-n-propyl methyl ether;* $\bar{C}$ with propylene + $BiCl_3$ similarly gives (63) γ-chloro-*n*-butyl methyl ether; $\bar{C}$ with 2-methylpropene-1 (isobutylene) + $HgCl_2$ on stdg. in s.t. 4 days at room temp. gives (60% yield (64)) 2-chloro-4-methoxy-2-methylbutane, b.p. 136° at 751 mm. D_4^{20} = 0.9455, accompanied by some *ter*-butyl chloride (3:7045); but $\bar{C}$ with isobutylene + $TiCl_4$ as directed (65) gives the corresp. alc., viz., 3-chloro-3-methylbutanol-1; $\bar{C}$ with 2-methylbutene-2 (trimethylethylene) (1:8220) with $ZnCl_2$ as directed (63) or with $HgCl_2$ in s.t. at room temp. for 48 hrs. (64) gives (40% yield (64)) 2-chloro-4-methoxy-2,3-dimethylbutane, b.p. 153° at 761 mm., 46–46.5° at 14 mm., D_4^{20} = 0 9528, accompanied by some *ter*-AmCl (3:7220); $\bar{C}$ with cyclohexene (1:8070) + $ZnCl_2$ in CS_2 stirred 5 hrs. at 0°, then 3 hrs. at room temp., gives (28.7% yield (66)) cf. (64) (*o*-chlorocyclohexyl)methyl methyl ether (2-chloro-1-(methoxymethyl)cyclohexane), b.p. 88–91° at 17 mm., D_4^{20} = 1.1552 (66).]

[$\bar{C}$ with butadiene-1,3 + $ZnCl_2$ in s.t. at room temp. for 24 hrs. gives (70% yield (64)) a mixt. of 1-chloro-5-methoxypentene-2, b.p. 168° at 758 mm., 56° at 10 mm., D_4^{20} = 1.0022 (from 1,4- addn. (?)) + 3-chloro-5-methoxypentene-1, b.p. 148° at 756 mm., 35° at 10 mm., D_4^{20} = 0.9740 (from 1,2 addn. (?)) (note that these two prods. represent synionic mesomers); $\bar{C}$ with cyclohexadiene-1,3 (1:8057) + $HgCl_2$ under CO_2 at 0° stood 24 hrs. gives (38% yield (64)) (4-chlorocyclohexenyl)methyl methyl ether, b.p. 81° at 10 mm., D_4^{20} = 1.0636 (64).]

[$\bar{C}$ (1 mole) + vinylacetylene (1 mole) + $BiCl_3$ (trace) + pyrogallol (trace) in dry ether at 5–15° for 9 hrs. (with periodic addns. of $BiCl_3$) gives (67) 34.8% yield 1-chloro-5- [illegible]-61° at 10 mm., D_4^{20} = 1.0427, n_D^{20} = 1.4893 (by 1,4 addn.), [illegible]hloro-5-methoxypentadiene-1,3, b.p. 46° at 10 mm., D_4^{20} = [illegible] with other prods.; note that of the two preceding dienes the former with Cu_2Cl_2 + HCl in ether at 20–40° for 2 hrs. readily isomerizes (81% yield (67)) to the latter; for further reactions of the pair see (67).]

[$\bar{C}$ with 4.67% dislvd. $ZnCl_2$ shaken with CO at 25–50° at 275–625 pounds press. for 8 hrs. gives (68) *methoxyacetyl chloride* (3:5225).]

C̄ with tertiary amines yields the corresp. quaternary ammonium salts: e.g., C̄ with Me_3N in dry ether gives (69) methoxymethyl-trimethyl-ammonium chloride (chloroplatinate, m.p. 228–229°, picrate, m.p. 198°); C̄ with pyridine in dry ether gives (69) methoxymethyl-pyridinium chloride (chloroplatinate, m.p. 182–185° (70), 180–182° dec. (35), $HgCl_2$ cpd., m.p. 91° (69)); C̄ with quinoline in $CHCl_3$ gives (69) methoxymethyl-quinolinium chloride (chloroplatinate, m.p. 232–234°; chloroaurate, m.p. 126–127°); for other quaternary salts see (69).

—— Methoxymethyl benzoate: oil, b.p. 283° (71). [From C̄ with NaOBz at 100° (71).]

—— Methoxymethyl *p*-nitrobenzoate: unreported.

—— Methoxymethyl 3,5-dinitrobenzoate: unreported.

—— *S*-(Methoxymethyl)isothiourea picrate: m.p. 163° (72). [From C̄ + thiourea in cold acetone giving (90% yield (72)) corresp. hydrochloride, m.p. 112° dec., which is then converted to the picrate.]

—— *N*-(Methoxymethyl)phthalimide: cryst. from dry MeOH, m.p. 120–121° (73), 118° (74). [Prepn. reported only by indirect means (73) (74).]

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Breslaue [illegible]
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(41) P [illegible]
(43) Smi [illegible]
Halmos, [illegible]
Nenitzes [illegible]
Simonsen, Storey, *J. Chem. Soc.* **95**, 2108–2109, 2111–2112 (1909). (49) Schlenk, Bergmann, *Ann.* **464**, 17–18 (1928). (50) Bergmann, *J. Chem. Soc.* **1936**, 412.

(51) de [illegible] (1941); *Cent.* **1942** [illegible] 2–463; *Compt. ren*[illegible] (4) **3**, 254–258 ([illegible] *ll. soc. chim.* (4) **39**, 989 (1926). (57) Chuit, *Helv. Chim. Acta* **9**, 268 (1926). (58) Yvon, *Compt. rend.* **180**, 748–749 (1925); *Cent.* **1925**, II 17. (59) Reychler, *Bull. soc. chim.* (4) **1**, 1198–1200 (1907). (60) Bottomley, Lapworth, Walton, *J. Chem. Soc.* **1930**, 2215–2216.

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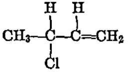
3:7090 *d,l*-3-CHLOROBUTENE-1 (γ-Chloro-α-butylene; α-methylallyl chloride)



C_4H_7Cl Beil. I — I_1— I_2-(174)

B.P.			
63°	**at 760 mm.**	**(1)**	D_4^{20} = **0.9001 (1)** n_D^{20} = **1.4151 (10)**
64–65°		**(2)**	**1.4150 (5) (3) (2)**
64°	**at 750 mm.**	**(5)**	**1.4153 (1)**
63.5°	**at 750 mm.**	**(3)**	**1.4242 (4)**
63.4–63.5°	**at 751 mm.**	**(10)**	
24.2–24.6°	**at 178 mm.**	**(3)**	
−5°	**at 26 mm.**	**(4)**	

For important discussion of the relationship and conversion of C̄ to 1-chlorobutene-2 see the latter (3:7205).

[For the prepn. of a mixt. of C̄ and 1-chlorobutene-2 from butadiene-1,3 + HCl see (5) (1) (6) (7); for prepn. of C̄ from methyl-vinyl-carbinol (buten-1-ol-3) + conc. HCl see (3) (4) (8).]

[For study of reaction with Mg, Zn, etc., see (9); for study of hydrolysis under various conditions see (10); for behavior with cuprous cyanide see (11).]

—— Methyl-vinyl-carbinyl *p*-nitrobenzoate: m.p. 43–44° (12). [Note that this prod. has been prepd. only by indirect means (12) and may (because of allylic rearr.) possibly be in fact crotonyl *p*-nitrobenzoate (see under 3:7205).]

—— *Methyl-vinyl-carbinyl 3,5-dinitrobenzoate: unreported.* [See also note under 3:7205.]

—— *N*-(Methyl-vinyl-carbinyl)phthalimide: m.p. 87–88° (13). [Prepd. indirectly, and structure unproved (13).]

3:7090 (1) Henne, Chanan, Turk, *J. Am.*
Bull. soc. chim. Belg. **31**, 168 (1922). (3)
(1942). (4) Böhme, *Ber.* **71**, 2378–2379
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Pont), U.S. 2,123,504, July 12, 1938; *Cent*
J. Indian Chem. Soc. **13**, 584 (1936). (9) Y
(10) Young, Andrews, *J. Am. Chem. Soc.* **66**, 421–425 (1944).
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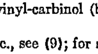
3:7100 3-CHLOROPROPYNE-1 (Propargyl chloride)



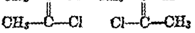
C_3H_3Cl Beil. I - 248 I_1— I_2—

B.P. 65° (1) D_-^5 = **1.0454 (1)**

[For prepn. from propyn-2-ol-1 (propargyl alcohol) [Beil. I-454, I_1-(234) with PCl_3 see (1) (2).]

3:7100 (1) Henry, *Ber.* 8, 398 (1875). (2) Pauling, Gordy, Saylor, *J. Am. Chem. Soc.* 64, 1753–1756 (1942).

3:7105 2-CHLOROBUTENE-2 C_4H_7Cl Beil. S. N. 11



cis *trans*

cis Stereoisomer

B.P.		F.P.		
66.6–67.0° at 760 mm.	(1)	−117.3° (18)	D_4^{20} = 0.9239 (18)	n_D^{20} = 1.4240 (18)
70.58°	(18)		D_4^{15} = 0.9246 (1)	
			D_4^{0} = 0.9420 (1)	$n_D^{13.4}$ = 1.4250 (1)

trans Stereoisomer

B.P.		F.P.		
62.4–62.8° at 760 mm.	(1)	−105.8° (18)	D_4^{20} = 0.9139 (18)	n_D^{20} = 1.4190 (18)
62.84°	(18)		D_4^{15} = 0.9185 (1)	
			D_4^{0} = 0.9361 (1)	$n_D^{13.4}$ = 1.4217 (1)

Ordinary C̄ (mixt.)

B.P.			
64–68°	(2)	D_4^{20} = 0.9179 (3)	
62–67°	(3)		n_D^{15} = 1.4232 (2)
59–61° at 761 mm.	(4)	D_4^{15} = 0.9220 (2)	

Both stereoisomers form with abs. EtOH const.-boilg. mixts from which C̄ can be recovered by repeated shaking with 3 vols. aq. to remove the alc., the azeotrope with *cis*-C̄, b.p. 60.0–60.4° at 760 mm., D_4^{15} = 0.8964, conts. 81.6% by wt. of *cis*-C̄, the azeotrope with *trans*-C̄, b.p. 56.8–57.2° at 760 mm., D_4^{15} = 0.8960, conts. 84.6% by wt. of *trans*-C̄ (1).

[For study of toxicity of C̄ see (5); for use as anthelmintic see (6).]

[For prepn. of the two geom. stereoisomers of C̄ from either *d,l*- (3:7615) or *meso*- (3:7580) 2,3-dichlorobutane with alc. KOH (1 mole + 25% excess) refluxed for 3 days see (1).]

[For prepn. of ord. C̄ (mixt. of *cis* + *trans* stereoisomers) from 2,2-dichlorobutane (3:7415) with alc. KOH see (8), from ord 2,3-dichlorobutane (3:7615) with alc. KOH (1) (2) (3) (8) (9), with aq. $NaHCO_3$ + Na_2CO_3 under press. (yield 20% C̄ accompanied by 4% butanone-2 (ethyl methyl ketone) (1:5405) + 5% butenols) (7), with aq. alkali or alkaline-earth hydroxides under press. at 118–250° (10), by passing vapor over $BaCl_2$ at 200–300° (11), or by passing vapor + steam at 300–400° over silica gel contg. $MgCl_2$ + $CaCl_2$, etc. (yields 21–25% C̄ accompanied by 35–38% butadiene-1,3 and 6–8% butanone-2) (3) see indic. refs.; from butanone-2 (ethyl methyl ketone) (1:5405) with PCl_5 (C̄ is accompanied by 2-chlorobutene-1 (3:7075) (12) and by 2,2-dichlorobutane (3:7415) (4)) see indic. refs.]

[For prepn. of C̄ from 2,2-dichloro-3-iodobutane (see below) with alc. KOH see (2); from 2-bromo-2-chloro-3-iodobutane with alc. KOH see (2) (note that the isomeric 2-bromo-3-chloro-2-iodobutane under same circumstances gives 3-bromo-2-chlorobutene-2).]

[For prepn. of C̄ from 2,3-dichlorobutene-2 (3:5500) with aq. alk. or alkaline-earth hydroxides under press. at 118–250° see (13).]

[C̄ with Cl_2 may *add* halogen, or be further *substituted* by halogen, or both, according to

circumstances: e.g., C̄ in liq. phase with Cl_2 at 20–40° in absence of light but in pres. of cat. *such as $SnCl_4$ or $FeCl_3$ adds Cl_2 giving (14) 2,2,3-trichlorobutane (3:5680);* C̄ in liq. phase with Cl_2 in pres. of light and of O_2 (15) or C̄ with Cl_2 in pres. of $NaHCO_3$ at 0° (4) substitutes further giving (55% *yield* (4)) (15) 2,3-dichlorobutene-1 (3:9074) (accompanied by 45% 2,2,3-trichlorobutane (3:5680) (4)); C̄ with Cl_2 at 350° gives (16) a mixt. of unsatd. chlorobutenes, probably 1,2-dichlorobutene-2 (3:5300) or (3:5615) and 1,3(2,4)-dichlorobutene-2 (3:5550).]

C̄ adds Br_2 yielding (2) 2,3-dibromo-2-chlorobutane, b.p. 182.5–186° sl. dec., 66–66.5° at 12 mm., D_4^{15} = 1.8975, n_D^{15} = 1.5339 (2) (this prod. with alc. KOH loses HBr yielding (2) 3-bromo-2-chlorobutene-2, b.p. 128–129.5°, D_4^{15} = 1.4998, n_D^{15} = 1.4950 (2)).

[C̄ adds ICl yielding (2) 2,2-dichloro-3-iodobutane, b.p. 69.5° at 11.5 mm., D_4^{15} = 1.8580, n_D^{15} = 1.5505 (2) (this prod. with KOH regenerates C̄).]

[*C̄ also adds HOCl but from the addn. prod. HCl splits out immediately: e.g., C̄ in CCl_4* with Cl_2 + aq. as directed (17) gives (85% yield (17)) 3-chlorobutanone-2 (α-chloroethyl methyl ketone) (3:7598).]

[For behavior of C̄ with dry HF yielding 2,2-difluorobutane see (18).]

[C̄ with steam passed at 300–400° over silica gel contg. $MgCl_2$ + $CaCl_2$ is unchanged (3) (dif. from 3-chlorobutene-1 (3:7090) or 1-chlorobutene-2 (3:7205) which lose HCl yielding butadiene-1,3 (3)). — Note that with alc. KOH the *cis*-C̄ splits off HCl 2.5 times as fast as the *trans*-C̄ (1).] [For dehydrohalogenation of C̄ yielding butadiene-1,3 see (19) (20).]

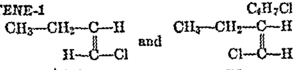
[C̄ with alcoholates or phenolates as directed (9) yields the corresp. ethers; e.g., C̄ with NaOEt yields (9) α,β-dimethylvinyl ethyl ether.]

C̄ on oxidn. with boilg. aq. $KMnO_4$ *yields (12) acetic acid (1:1010) and propionic acid* (1:1025); the *cis*-C̄ appears to give mainly acetic acid; the *trans*-C̄ gives mainly propionic acid (12).

3:7105 (1) Naves, *Bull. soc. chim. Belg.* 39, 435–443 (1930); *Cent.* **1931**, I 1269–1270; *C.A.* **25**, 2412 (1931). (2) Petrov, Sapozhnikova, *J. Gen. Chem. (U.S.S.R.)* 7, 476–484 (1937); *Cent.* **1937**, I 4025; *C.A.* **31**, 4263 (1937). (3) Gutner, Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 6, 1729–1735 (1936); *Cent.* **1937**, I 3780; *C.A.* **31**, 4265 (1937). (4) Tishchenko, *J. Gen. Chem. (U.S.S.R.)* 8, 1232–1246 (1938); *Cent.* **1939**, II 4222–4223, *C.A.* **33**, 4190 (1939). (5) McCawley, *Univ. Calif. Pub. Pharmacol.* 2, 89–97 (1942); *C.A.* 36, 4011 (1942). (6) Marcenac, *Compt. rend.* 198, 510–512 (1934); *Cent.* **1934**, I 2780; *C.A.* 28, 2800 (1934). (7) Dobryanskii, Gutner, Shchigel'skaya, *J. Gen. Chem. (U.S.S.R.)* 7, 1315–1320 (1937); *Cent.* **1938**, I 561, *C.A.* **31**, 6189 (1937). (8) Tishchenko, Churbakov, *J. Gen. Chem. (U.S.S.R.)* 7, 663–666 (1937); *Cent.* **1937**, II 372; *C.A.* **31**, 5754 (1937). (9) I.G., Brit. 332,005, Aug. 21, 1930; *Cent.* **1930**, II 2572. (10) du Pont Co. & Cass, Brit. 549,790, Dec. 8, 1942; *C.A.* **38**, 750 (1944).

(11) Levine, Cass (to du Pont Co.), U.S. 2,323,226, June 29, 1943; *C.A.* **38**, 110 (1944); Brit. 535,585, April 15, 1941; *C.A.* **36**, 1337 (1942). (12) Charpentier, *Bull. soc. chim.* (5) 1, 1407–1411 (1934). (13) Cass (to du Pont Co.), U.S. 2,291,375, July 28, 1942; *C.A.* **37**, 656 (1943). (14) Levine, Cass (to du Pont Co.), U.S. 2,323,227, June 29, 1943; *C.A.* **38**, 110 (1944); Brit. 535,586, April 15, 1941; *C.A.* **36**, 1337 (1942). (15) Hearne (to Shell Development Co.), U.S. 2,296,614, Sept. 22, 1942; *C.A.* **37**, 1129 (1943). (16) N. V. de Bataafsche Petroleum Maatschappij, Brit. 468,010, July 22, 1937; *Cent.* **1937**, II 4102; *C.A.* **31**, 8543 (1937); French 810,112, March 15, 1937; *Cent.* **1937**, II 4102; *C.A.* **32**, 587 (1938). (17) Groll, Hearne (to Shell Development Co.), *U.S. 2,060,303, Nov. 10, 1936; Cent.* **1937**, *I 4154; C.A.* **31**, 419 (1937); Brit. 437,573, Nov. 28, 1935; French 787,529, Sept. 24, 1935; *Cent.* **1936**, II 2227. (18) Henne, Hinkamp, *J. Am. Chem. Soc.* **67**, 1194–1197 (1945). (19) Evans, Morris, Melchior (to Shell Development Co.), U.S. 2,379,697, July 3, 1945; *C.A.* **39**, 4331 (1945). (20) Hearne (to Shell Development Co.), U.S. 2,379,708, July 3, 1945; *C.A.* **39**, 4330 (1945).

3:7110 1-CHLOROBUTENE-1 C_4H_7Cl Beil. S. N. 11



trans *cis*

trans Stereoisomer

B.P.		
68.0–68.2° at 760 mm. (1)	D_4^{15} = 0.9205 (1)	$n_D^{14.6}$ = 1.4225 (1)
	D_4^0 = 0.9376 (1)	

cis Stereoisomer

B.P.		
63.4–63.6° at 760 mm. (1)	D_4^{15} = 0.9153 (1)	n_D^{15} = 1.4194 (1)
	D_4^0 = 0.9329 (1)	

Both stereoisomers form with abs. EtOH const.-boil. mixts from which C̄ can be recovered by repeated shaking with 3 vols. aq. to remove the alc.: the azeotrope with the *trans* form, b.p. 61.2–61 6° at 760 mm, D_4^{15} = 0.8912, conts. 79 8% by wt. of C̄; the azeotrope with the *cis* form, b.p. 57.0–58.2° at 760 mm, D_4^{15} = 0.8946, conts. 85.2% by wt. of C̄ (1).

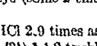
[For formn of both *trans* and *cis* forms of C̄ from *d,l*-1,2-dichlorobutane (3:7680) with alc. KOH (1 mole + 25% excess) refluxed 3 days (some 2-chlorobutene-1 (3:7075) is also formed) see (1).]

[The *cis* form of C̄ with alc. KOH splits off HCl 2.9 times as fast as the *trans* form (1).]

[*C̄ with Cl_2 in dark at 10° gives (70–75% yield (2)) 1,1,2-trichlorobutane, but no constants for latter can be found either in (2) or in prior literature.*]

3:7110 (1) Navez, *Bull. soc. chim. Belg.* **39**, 435–443 (1930), *Cent.* **1931**, I 1269–1270; *C.A.* **25**, 2412 (1931) (2) Henne, Hinkamp *J Am Chem Soc.* **67**, 1197 (1945).

3:7120 1-CHLORO-2-METHYLPROPENE-1 C_4H_7Cl Beil. I - 209
(β,β-Dimethylvinyl chloride; I_1—
isocrotyl chloride; I_2—
α-chloroisobutylene)



B.P.			
68–69° at 775 mm.	(1)	D_{25}^{25} = 0.9144 (3)	n_D^{25} = 1.4198 (3)
68.1°	(2) (5)		
66.9° at 757 mm.	(3)	D_4^{20} = 0.9186 (2)	n_D^{20} = 1.4221 (2)
65–68°	(4)	0.918 (6)	1.422 (7)

[*See also 3-chloro-2-methylpropene-1* (3:7145).]

Note that for C̄ the designation β,β-dimethylvinyl chloride is now preferred, cf. (5); great care should be used to avoid confusion of C̄ with the isomeric and very closely related 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145); both these compounds are now commercial chemicals in the U.S.A.

[For prepn. of C̄ from 3-chloro-2-methylpropene-1 (methallyl chloride) (3:7145) see (2) (8): e.g., methallyl chloride (10 moles) with 80% H_2SO_4 (1 mole) stirred at 40° for 2½ hrs. gives an upper phase contg 87% C̄ + 7% residual methallyl chloride + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85% C̄ (8) (20).]

[For formn. of C̄ (usually accompanied by the isomeric methallyl chloride and/or other

prods.) from 2-methylpropene-1 (isobutylene) with Cl_2 (5) (9); from 1,1-dichloro-2-methylpropane (isobutylidene dichloride) (3:7425) by actn. of NH_4OH or alc. KOH (4), from 1,2-dichloro-2-methylpropane (isobutylene dichloride) (3:7430) with alc. KOH (10) see indic. refs.]

[For formn. of $\bar{C}$ (together with the isomeric methallyl chloride) from 1-chloro-2-methylpropanol-2 (isobutylene chlorohydrin) (3:7752) by soln. in cold 45% H_2SO_4 and subsequent warming (giving 90% $\bar{C}$ + 10% methallyl chloride (2) (8)), or by use of P_2O_5 (11) cf. (12); from 1,1,1-trichloro-2-methylpropanol-2 (1,1,1-trichloro-*ter*-butyl alc. = "Chloretone") (3:2662) with Zn dust + boilg. alc. (13), or from isobutyraldehyde (1:0120) by actn. of PCl_5 (4) see indic. refs.]

$\bar{C}$ forms with aq. a const.-boilg. mixt., b.p. 61.9°, contg. 7.5% aq. (2)

[For study of anesthetic props. of $\bar{C}$ see (14).]

Reactions involving further substitution of H atoms in $\bar{C}$. [$\bar{C}$ with Cl_2 (in pres. of 1.5 moles $NaHCO_3$ at 0° (15)) cf. (2) reacts not only by addn. but *also* by substitution (the latter involving a shift of double bond) giving respectively 32% 1,1,2-trichloro-2-methylpropane (3:5710) + 68% 1,1-dichloro-2-methylpropene-2 (3:7480).]

Reactions involving the double bond of $\bar{C}$. [$\bar{C}$ adds Cl_2 (see preceding paragraph).]

[*$\bar{C}$ also adds HOCl (chlorohydrination)*; e.g., $\bar{C}$ with Cl_2 + aq., or aq. HOCl, or even alkyl or aralkyl hypochlorites as directed (16) cf. (2) (4), yields 1,1-dichloro-2-methylpropanol-2 (β,β-dichloro-*ter*-butyl alc.) (3:5772), b.p. 150°.]

[$\bar{C}$ can also undergo catalytic hydration of the double bond: e.g., $\bar{C}$ (1 mole) with 90% H_2SO_4 (1 mole) stirred at −10° to 0° for 2½ hrs., then poured onto cracked ice, diluted with aq., and distilled, gives 66% of the initial $\bar{C}$ as 1-chloro-2-methylpropanol-2 (β-chloro-*ter*-butyl alcohol) (isobutylene chlorohydrin) (3:7752); note that other acids can also be used for this hydration, e.g., 85% H_3PO_4, 70% HNO_3, 60% $HClO_4$, benzenesulfonic acid, e.g., each having its own optimum conditions. Note also that some 18% of the initial $\bar{C}$ is not hydrated but is partially isomerized to a mixt. contg. 90% $\bar{C}$ + 10% methallyl chloride (2) (17).]

Reactions involving the halogen atom of $\bar{C}$. Note that in $\bar{C}$ the halogen is *extremely* inert as compared with that of the isomeric methallyl chloride (3:7145); this permits removal of the latter from $\bar{C}$ by chemical means (see below).

[$\bar{C}$ is virtually unattacked by aq. or alc. KOH even at 100° (11) (1) (2) (dif. from methallyl chloride (3:7145)). — $\bar{C}$ does not react with boilg. aq. K_2CO_3 or KOAc (1) (dif. from methallyl chloride (3:7145)).]

[$\bar{C}$ is not normally convertible to isobutyraldehyde except under extreme conditions (5) (dif. from methallyl chloride (3:7145) which upon acid hydrolysis or even boilg. with aq. gives isobutyraldehyde).]

—— β,β-Dimethylvinyl (isocrotyl) acetate: unreported.
—— β,β-Dimethylvinyl (isocrotyl) benzoate: unreported.
—— β,β-Dimethylvinyl (isocrotyl) *p*-nitrobenzoate: unreported.
—— β,β-Dimethylvinyl (isocrotyl) 3,5-dinitrobenzoate: unreported.
—— *N*-(β,β-dimethylvinyl)phthalimide: unreported.

3:7120 (1) Pogorshelski, *J. Russ. Phys.-Chem. Soc.* **36**, 1129-1184 (1904); *Cent.* **1905**, I 667-668. (2) Burgin, Hearne, Rust, *Ind. Eng. Chem.* **33**, 385-388 (1941). (3) Hurdis, Smyth, *J. Am. Chem. Soc.* **65**, 89 (1943). (4) Oeconomides, *Compt. rend.* **92**, 1237 (1881); *Bull. soc. chim.* (2) **35**, 499-500 (1881). (5) Burgin, Engs, Groll, Hearne, *Ind. Eng. Chem.* **31**, 1413-1419 (1939). (6) Engs, Redmond, U.S. 2,077,382, April 20, 1937; *Cent.* **1937**, II 1660; *C.A.* **31**, 3937 (1937). (7) Aschan, *Oversikt Finska Vetenskaps-Soc. Förh.* **58**, 122 (1916). (8) Groll, Burgin (to Shell Development Co.), U.S. 2,042,223, May 26, 1936; *Cent.* **1937**, I 1274; *C.A.* **30**, 4875 (1936). (9) Tamele, Ott, Marple, Hearne, *Ind. Eng. Chem.* **33**, 115 (1941). (10) Mouneyrat, *Ann. chim.* (7) **20**, 533-534 (1900).

(11) Michael, *J. prakt. Chem.* (2) **64**, 104 (1901). (12) Krassuski, *J. prakt. Chem.* (2) **64**, 390 (1901); *J. Russ. Phys.-Chem. Soc.* **33**, 1-26 (1901); *Cent.* **1901**, I 996. (13) Jozitsch, *J. Russ. Phys.-Chem. Soc.* **30**, 920-924 (1898); *Cent.* **1899**, I 606. (14) Abreu, Peoples, Emerson, *Anesthesia and Analgesia* **18**, 156-161 (1939); *Cent.* **1939**, II 2111; *C.A.* **33**, 6959 (1939). (15) Tishchenko, *J. Gen. Chem (U.S.S.R.)* **8**, 1232-1245 (1938), *Cent.* **1939**, II 4222; *C.A.* **33**, 4190 (1939). (16) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* **1937**, I 4154; *C.A.* **31**, 419 (1937). N. V. de Bataafsche Petroleum Matschappij., Brit. 437,573, Oct. 31, 1935; *Cent.* **1936**, II 2227; *C.A.* **30**, 2199 (1936), French 787,529, Sept. 24, 1935; *Cent.* **1936**, II 2227; *C.A.* **30**, 1067 (1936). (17) Groll, Burgin (to Shell Development Co.), U.S. 2,042,222, May 26, 1936; *Cent.* **1937**, I 1546, *C.A.* **30**, 4875 (1936); N. V. de Bataafsche Petroleum Matschappij, French 791,644, Dec. 14, 1935, *Cent.* **1936**, II 2227.

3:7125 *d,l*-2-CHLOROBUTANE (*sec.*-Butyl chloride; ethyl-methyl-carbinyl chloride) — C_4H_9Cl — $CH_3—CH_2—CH(Cl)—CH_3$ — Beil. I - **119**; I_1—; I_2-(81)

B.P.			F.P.		
68.4-68.6° u.c.		(28)	**−131.3°** (1) (10)	D_4^{25} = **0.86767** (1)	
68.25°	at 760 mm.	(1) (2)			
68.1°		(3)		D_4^{20} = **0.8740** (5)	
68.0-68.1°		(4)		**0.87323** (1)	
68°	at 761 mm.	(5)		**0.8726** (5)	
68°	at 769 mm.	(5)		**0.8707** (6)	
67.3-67.8°	cor.	(6)			
67.3°	at 761.4 mm.	(7)		D_4^{15} = **0.87880** (1)	
67.2-67.3°	at 740 mm.	(4)			$n_D^{25.2}$ = **1.3953** (11)
67.2-67.7°	at 734 mm.	(8)			
67.2°	at 764 mm.	(7)			n_D^{20} = **1.39709** (5)
66.5°	at 731.8 mm.	(9)			**1.39694** (5)
					1.3969 (3)
(For b.p. of C at various press. in range 49-285 mm. see (2).)					n_D^{15} = **1.3994** (1)

Liquid with agreeable ethereal odor.

[For prepn. of $\bar{C}$ from butanol-2 (1:6155) by saturation with dry HCl gas and htg. in s.t. at 100° for several hrs. (9); by distillation with 18 wt. pts. 6 *N* HCl (50% yield (12)); with conc. HCl + $ZnCl_2$ (2 moles) (yields: 85-88% (13), 83% (14), 82% (5), 78% (15), 60-68% (16) (17)) (6); with PCl_3 + $ZnCl_2$ (yields: 67% (15), 40% (6)); with PCl_5 + $ZnCl_2$ (71% yield (15)); with $SOCl_2$ + pyridine (yields: 90% (15), 47% (5)); or with HCl in pres. of H_3PO_4 (18) see indic. refs.]

[For formn. of $\bar{C}$ from either butene-1 or butene-2 with HCl gas by addn. to unsatd. linkage (7) (19) in pres. of cat. (20) (21) (22) see indic. refs.; from *n*-butane with Cl_2 see (4) (23); from *n*-butylamine with HNO_2 (2.8% yield $\bar{C}$ accompanied by 36.5% butenes, 25% butanol-1, 13.2% butanol-2, 5.2% *n*-butyl chloride (3:7160) and other prods.) see (24); from *sec.*-butylamine with NOCl in xylene see (25).]

[For study of anthelmintic props. of $\bar{C}$ see (26).]

Pyrolysis of $\bar{C}$. [$\bar{C}$ at 450-550° without cat. loses HCl and yields (4) (27) a mixt. contg. butene-1, *cis*-butene-2, and *trans*-butene-2 (dif. from 1-chlorobutane (3:7160) which gives only butene-1); $\bar{C}$ at 450° in pres. of anhyd. $CaCl_2$ as cat. gives (4) (27) the same mixt. (as does also 1-chlorobutane (3:7160)). For use of this pyrolysis in distinction of $\bar{C}$ from *ter*-butyl chloride (3:7045) see (23).]

Further halogenation of C̄. [C̄ with Cl_2 at 200–380° gives (28) a mixt. of dichlorobutanes contg. 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and *d,l*-2,3-dichlorobutane (3:7615) but no 1,2-dichlorobutane (3:7680); note, however, that C̄ with Cl_2 in pres. of light gives (29) 1,2-dichlorobutane (3:7680), 1,3-dichlorobutane (3:7925), 2,2-dichlorobutane (3:7415), and both *d,l*- (3:7615) and *meso*- (3:7580) 2,3-dichlorobutanes.]

Reactions of the halogen atom of C̄. [For study of rate of reactn. of C̄ with KI in acetone at 60° see (30).]

[C̄ with C_6H_6 + $AlCl_3$ gives (yields: 82.5% (9), 69% (31)) *sec.*-butylbenzene (1:7490); C̄ with C_6H_6 + Al/Hg gives (59.5% yield (32)) *ter*-butylbenzene (1:7460); C̄ with naphthalene + AlHg gives (48% yield (32)) 1-(*sec.*-butyl)naphthalene.]

[C̄ with acetanilide + $AlCl_3$ in ethylene dichloride (3:5130) at −5° gives (33) *N*-acetyl-*p*-(*sec.*-butyl)aniline, cryst. from di-isopropyl ether, m.p. 121–122° (33).]

C̄ with Mg in dry ether gives (87% yield (34)) *sec.*-BuMgCl (see also below).

Ⓓ Ethyl-methyl-acetic acid (1:1105): b.p. 176–177°. [From C̄ by conversion to RMgCl and carbonation of the latter with CO_2 (yields: 76–86% (35), 72%) (by adding ether soln. directly to solid CO_2 (36)).]

Ⓓ Ethyl-methyl-acetic anilide: m.p. 110–111° (37), 108° u.c. (38), 105.5–106.5° u.c. (39). [From C̄ (39) (24) or *sec.*-BuBr (38) by conversion to RMgX and reactn. in dry ether with phenyl isocyanate.] [Note that this prod. does not distinguish C̄ from ethyl chloride (3:7015) or from isopropyl chloride (3:7025) for which the corresp. anilides melt at 104–104.5°; moreover, it is not recommended as distinction from isobutyl chloride (3:7135) for which the corresp. isovaleranilide has m.p. 109–110° u.c. (39).]

Ⓓ Ethyl-methyl-acetic-*p*-toluidide: m.p. 92.5–93° u.c. (39). [From C̄ by conversion to RMgCl (see above) and reactn in dry ether with *p*-tolyl isocyanate (39).]

Ⓓ Ethyl-methyl-acetic α-naphthalide: m p. 128–129° u.c. (39). [From C̄ by conversion to RMgCl (see above) and reactn. in dry ether with α-naphthyl isocyanate (39).] [Note that this prod. does not distinguish C̄ from isobutyl chloride (3:7135) for which the corresp. isovalero-α-naphthalide has m.p. 125–126° u.c. (39).]

—— *sec.*-Butyl mercuric chloride (*sec.*-BuHgCl): cryst. from alc., m.p. 30.5° (40). [Reported only by indirect means (40).]

—— *S*-(*sec.*-Butyl)isothiourea picrate: m.p. 190° (41). [Not reported from C̄ but obtd. from *sec.*-BuBr (0.2 g.) + thiourea (0.2 g.) refluxed in alc. (2 ml.) for 2 min., then treated with PkOH (0.2 g.) dislvd. in least possible hot alc. (41).]

—— *N*-(*sec.*-Butyl)phthalimide (2-(*N*-phthalimido)butane): m.p. 24.5–25.5° (42). [Not reported from C̄ but obtd. (35% yield (42)) from *sec.*-BuBr with K phthalimide by htg. in s t. at 210° for 4 hrs.; note that m.p. is too low to be recommended as deriv. for identification.]

—— *N*-(*sec.*-Butyl)-3-nitrophthalimide: unreported.

—— *N*-(*sec.*-Butyl)tetrachlorophthalimide: unreported.

—— *N*-(*sec.*-Butyl)-*o*-sulfobenzoic imide (*N*-(*sec.*-butyl)saccharin): m.p. 81° (43). [Not reported from C̄ but obtd. from *sec.*-BuBr or *sec.*-BuI with sodium saccharin in aq. butylcarbitol (1·6517) on refluxing for 30 min. (43).]

—— *N*-(*sec.*-Butyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide: unreported.

—— *p*-(*sec.*-Butoxy)benzoic acid: m.p. 121–123° u.c. (44). [From C̄ (7) or from *sec.*-BuBr with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (44).] [Note, however, that this prod. does not distinguish C̄ from the corresp. deriv. of *n*-amyl chloride (3:7460) whose m.p. is 123–124° u.c. (44).]

—— *sec.*-Butyl 2,4,6-triiodophenyl ether: unreported.

—— *sec.*-Butyl α-naphthyl ether: b.p. 293.5° cor. (45). (Corresp. picrate, m.p. 100.5–101.0° cor.; Neut. Eq. calcd. 429, found 427 (45).)

—— *sec.*-Butyl β-naphthyl ether: b p. 298.5° cor. (45), 298° (46). (Corresp. picrate, m p. 86.0–86 5° cor (45); 85° (46); Neut. Eq., calcd. 429, found 429 (46).)

3:7125 (1) Timmermans, Martin, *J. chim. phys* **25**, 424–425 (1927). (2) Roland, *Bull soc. chim. Belg.* **37**, 122 (1928). (3) Wiswall, Smyth, *J. Chem Phys.* **9**, 357 (1941). (4) Weston, Hass, *J. Am Chem. Soc.* **54**, 3337–3343 (1932). (5) Vogel, *J Chem Soc* **1943**, 638–639. (6) Norris, Green, *Am. Chem. J.* **26**, 307–308 (1901). (7) Coffin, Sutherland, Maass, *Can. J. Research* **2**, 267–278 (1930), *Cent.* **1930**, II 2250, *C.A* **24**, 3750 (1930). (8) Dadieu, Pongratz, Kohlrausch, *Monatsh.* **61**, 416 (1932) (9) Estreicher, *Ber.* **33**, 438–441 (1900) (10) Timmermans, *Bull. soc. chim. Belg* **36**, 504 (1927).

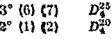
(11) Wendell, *Am Chem. J.* **26**, 318 (1901) (12) Norris, *Am Chem. J* **38**, 641–642 (1907). (13) Copenhaver, Whaley, *Org Syntheses*, Coll. Vol. **1** (2nd ed.), 143, espec. Note 6 (1941). (14) Whaley, Copenhaver, *J Am. Chem. Soc* **60**, 2497–2498 (1938). (15) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (16) Norris, *Org. Syntheses*, Coll. Vol. **1** (1st ed.), 137–138 (1932), **5**, 28, Note 5 (1925). (17) Norris, Taylor, *J. Am Chem. Soc* **46**, 756 (1924). (18) A. Wacker Soc. Elektrochem. Ind, French 687,855, Aug. 14, 1930; *Cent.* **1930**, II 3637; *C.A.* **25**, 709 (1931). (19) Coffin, Maass, *Can J Research* **3**, 526–539 (1930), *Cent* **1931**, I 2430; *C.A.* **25**, 1146–1147 (1931). (20) Strange, Kane, Brit. 500,880, March 16, 1939; *Cent.* **1939**, II 226, *C.A* **33**, 5867 (1939).

(21) Kane (to Strange), U.S. 2,119,167, May 31, 1938, *C A* **32**, 5413; Brit. 414,766, Sept. 6, 1934; French 769,103, Aug. 20, 1934, *Cent* **1935**, I 1934. (22) Winkler, Ger. 574,802, March 30, 1933; *Cent.* **1933**, I 3497 (23) Hass, McBee, Weber, *Ind Eng. Chem.* **27**, 1190–1195 (1935). (24) Whitmore, Langlois, *J. Am Chem Soc* **54**, 3441–3447 (1932) (25) Ssolonina, *J. Russ. Phys-Chem Soc* **30**, 431–449 (1898), *Cent.* **1898**, II 888 (26) Wright, Schaffer, *Am J. Hyg.* **16**, 325–428 (1932); *Cent.* **1932**, II 3119, *J Parasitol.* **16**, 107–108 (1929); *C.A.* **26**, 4869 (1932). (27) Hass, Weston (to Purdue Research Foundation), U.S. 1,975,456, Oct 2, 1934, *Cent.* **1935**, II 2880, *C.A.* **28**, 7260 (1934). (28) Rust, Vaughan, *J. Org. Chem.* **6**, 479–488 (1941). (29) Tishchenko, Churbakov, *J Gen Chem.* (*U.S.S.R*) **7**, 663–666 (1937), *Cent.* **1937**, II 372, *C A.* **31**, 5754 (1937). (30) Conant, Hussey, *J. Am Chem Soc.* **47**, 485 (1925).

(31) Boedtker, *Bull soc. chim.* (4) **45**, 649 (1929). (32) Duguid, *J. Am Chem Soc.* **63**, 3527–3528 (1941) (33) U.S. Industrial Alc. Co., French 811,832, April 23, 1937, *Cent* **1937**, II 1267; *C.A.* **32**, 593 (1938). (34) Whitmore, Badertscher, *J. Am Chem. Soc* **55**, 4159 (1933). (35) Gilman, Kirby, *Org Syntheses*, Coll. Vol. **1** (2nd ed.), 361–364 (1941); (1st ed), 353–356 (1932). (36) Bartlett, Stauffer, *J. Am Chem. Soc* **57**, 2582 (1935). (37) Verkade, *Rec. trav. chim* **36**, 204 (1916). (38) Schwartz, Johnson, *J. Am Chem. Soc.* **53**, 1063–1067 (1931). (39) Underwood, Gale, *J. Am Chem. Soc.* **56**, 2117–2120 (1934). (40) Marvel, Calvery, *J. Am. Chem Soc.* **45**, 821 (1923).

(41) Brown, Campbell, *J. Chem. Soc.* **1937**, 1699–1700 (42) Mumm, Richter, *Ber.* **73**, 855 (1940). (43) Merritt, Levey, Cutter, *J. Am. Chem. Soc.* **61**, 15–16 (1939). (44) Lauer, Sanders, Leekley, Ungnade, *J. Am. Chem. Soc.* **61**, 3050 (1939). (45) V. H. Dermer, O C. Dermer, *J. Org. Chem.* **3**, 290–291 (1938/39). (46) Wang, *J. Chinese Chem. Soc.* **1**, 61–62 (1933).

3:7135 1-CHLORO-2-METHYLPROPANE C_4H_9Cl Beil. I - 124
(Isobutyl chloride; I_1-(40)
isopropylcarbinyl chloride) I_2-(87)



B.P.			M.P.	
68.85°	at 760 mm.	(1) (2)	−130.3° (6) (7)	D_4^{25} = 0.87177 (1)
68.8–69.2°	at 769.2 mm.	(3)	−131.2° (1) (2)	D_4^{20} = 0.8810 (5)
68.5° cor.		(4)		0.87733 (1)
68.5° cor.	at 756 mm.	(5)		D_4^{15} = 0.88290 (1)
68.2°		(6) (7) (8)		

n_D^{25} = 1.39576 (1)
n_D^{20} = 1.39841 (5)
1.39836 (1)
1.3983 (8)
n_D^{15} = 1.40096 (1)
1.40047 (6)

Colorless liquid. — Very spar. sol. aq.; 100 ml. aq. at 12.5° dis. 0.092 g. C̄ (9).

C̄ forms with aq. a const-boilg. mixt. (consts. not reported (10)) (use in sepn. from *ter*-butyl alc. (1:6140) (10); C̄ also forms binary azeotropes with many org. compounds; e.g., C̄ with *EtOH* (1:6130) forms a const.-boilg. mixt., b.p. 61.45° at 760 mm., contg. 72 mole % C̄ (11); C̄ with *propanol-1* (1:6150) forms a const.-boilg. mixt., b.p. 67.7° at 760 mm., contg. 78 wt. % C̄ (12); C̄ with *propanol-2* (1:6135) forms a const.-boilg. mixt., b.p. 64.8° at 760 mm., contg 83 wt. % C̄ (13); C̄ with *ter-butyl alc.* (1:6140) forms a const.-boilg. mixt., b.p. 65.5° at 760 mm., contg. 83 wt. % C̄ (14); C̄ with *allyl alc.* (1:6145) forms a const.-boilg. mixt., b.p. 67.2° at 760 mm., contg. 93 wt. % C̄ (14); C̄ with *EtOH* (1:6130) + *aq.* forms a ternary const.-boilg. mixt., b.p. 58.62° at 760 mm. (2 phases), contg. 62.6 mole % C̄ + 19.8 mole % EtOH + 17.6 mole % aq. (11).

[For prepn. of C̄ from isobutyl alc. (1:6165) with dry HCl gas in s.t. at 120° for 8 hrs. (3) cf. (23) (gives 94% yield of a mixt. of C̄ + *ter*-butyl chloride (3:7045) from which latter can be removed by 5-hr. shaking with 10% aq. KOH (3)) cf. (22); with dry HCl gas at 100° for 10 hrs. (4) or in pres. of pyridine (15) or CdO, $ZnCl_2$ or other cat. (16); or over Al_2O_3 at 420° (*ter*-butyl chloride is also formed (17)); with conc. aq. HCl + $ZnCl_2$ refluxed 1 hr. (15% yield (18) (19)); with PCl_3 + $ZnCl_2$ (yields: 85% (20), 80% (18), 32% (21)) (note that some *ter*-butyl chloride is formed (21)); with PCl_5 (24) or PCl_5 + $ZnCl_2$ (76% yield (18)); or with $SOCl_2$ + pyridine (88% yield (18)) (5), $SOCl_2$ + dimethylaniline (70% yield (18)), $SOCl_2$ + diethylaniline (58% yield (18)) (note that use of aniline gives only 19% yield (18)) see indic. refs.]

[For formn. of C̄ from 2-methylpropane (isobutane) with Cl_2 + cat. at 180° (60% yield (25) together with other prods.) (26) see indic. refs.; for formn. of C̄ from isobutylene by cat. addn. of HCl (note "abnormal" addition) see (27).]

[For formn. of C̄ from isobutylamine with NOCl in xylene at −15° (28) or with aqua regia (29) see indic. refs.; from *n*-butyl acetate (1:3145) by pyrolysis with $AlCl_3$ see (30).]

[For sepn. of C̄ from *ter*-butyl chloride (3:7045) by hydrol. of latter with aq. alk. and extraction of the resultant *ter*-butyl alc. with aq. see (10) (3); for sepn. of C̄ from more reactive alkyl chlorides (such as *ter*-butyl chloride (3:7045), methallyl chloride (3:7145), etc.) by esterification of the reactive chlorides by htg. at 125–225° under press. in pres. of Cu with alkali salt of a suitable acid, followed by fractional distn., see (47).]

[C̄ on suitable htg dec. into isobutylene and HCl; if the process is so conducted that these prods. can react at lower temp. they combine to yield *ter*-butyl chloride (3:7045): e.g., C̄ passed over pumice at 500° (31), or over clay at 250–300° (32), or over $BaCl_2$, $ThCl_4$, ThO_2, *kaolin*, etc., at 300° (33) (34) (35) (36), or with H_2 over reduced *Ni at 270°* (35) (36) yields isobutylene + HCl; for execution of this process so as to permit recombination to *ter*-butyl chloride (3:7045) see (37). — Note that C̄ on htg. in s.t. at 306° for 6 hrs. gives (3) 8% *ter*-butyl chloride; for study of the equilibrium in the system C̄ + *ter*-butyl chloride + HCl over range 88–237° see (38).]

[C̄ with Cl_2 yields (39) (26) 1,3-dichloro-2-methylpropane (3:7960) and other prods. — C̄ with Br_2 (1 mole) in pres. of Fe in s.t. at 100° for 6 hrs. gives (40) 1,2-dibromo-2-methyl propane (isobutylene dibromide), b.p. 148° (40).]

[C̄ with aq. soln or susp of inorg. bases under press. at 120–350° yields (41) a mixt. contg isobutyl alc. (1:6165), *ter*-butyl alc. (1:6140), and isobutylene. — For study of rate of hydrolysis of C̄ in 50% alc. in pres. and abs. of dil. H_2SO_4 see (42). — In connection with hydrolysis of C̄ to isobutyl alc. note that these two form no azeotrope (1).]

[C̄ with Na in liq. NH_3 gives 2-methylpropane (isobutane) (43); but C̄ with $NaNH_2$ in liq. NH_3 gives isobutylene (43).]

[C̄ with C_6H_6 + $AlCl_3$ gives exclusively (44) (45) (46) (21) *ter*-butylbenzene (1:7460).]

C̄ with Mg in dry ether in pres. of trace of MeI as cat. gives in 8 hrs. (98.0% yield (48))

corresp. isobutyl MgCl; the ethereal soln. of this RMgCl undergoes the usual reactns. (see also below).

Ⓓ Isovaleric acid (1:1050) q.v. [From isobutyl MgCl with CO_2 followed by dil. non-volatile acid and subsequent distn. (49) (yield not reported).]

Ⓓ Isovaleranilide: m.p. 109–110° u.c. (50). [From isobutyl MgCl (above) with phenyl isocyanate in dry ether (50).] [Note that this derivative does *not* distinguish C̄ from isoamyl chloride (3:7365) or 2-chlorobutane (3:7125) q.v.]

Ⓓ Isovalero-*p*-toluidide: m.p. 106–107° u.c. (50). [From isobutyl MgCl (above) with *p*-tolyl isocyanate in dry ether (50).] [Note that this derivative does not distinguish C̄ from 3-chloropentane (3:7330) q.v., but that it is the best means of distinction from 2-chlorobutane (3:7125).]

Ⓓ Isovalero-α-naphthalide: m.p. 125–126° u.c. (50). [From isobutyl MgCl (above) with α-naphthyl isocyanate in dry ether (50).] [Note that this derivative does *not* distinguish C̄ from 2-chlorobutane (3:7125) q.v.]

—— Isobutyl mercuric chloride: unreported.

—— *S*-(Isobutyl)isothiourea picrate: m.p. 174° (51). [This prod. has been reported from isobutyl bromide (or iodide) (but not from C̄) by htg. with thiourea in alc. for 2 min., followed by addn. of alc. PhOH (51).]

—— *N*-(Isobutyl)phthalimide (1-(*N*-phthalimido)-2-methylpropane): lfts. from CS_2, m.p. 93° (53). [This prod. has been reported from isobutyl *bromide* with K phthalimide on htg. in s.t. at 210° for 3–4 hrs. (53).]

—— *N*-(Isobutyl)-3-nitrophthalimide: unreported.

—— *N*-(Isobutyl)tetrachlorophthalimide: unreported.

—— *N*-(Isobutyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide: cryst. from 75% alc., m.p. 78–79° (57). [From C̄ (?) or the corresp. isobutyl bromide with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidine in alc. KOH after 1 hr. refluxing (57).]

—— *N*-(Isobutyl)-*o*-sulfobenzoic imide (*N*-(isobutyl)saccharin: m.p. 75.0° (55). [Not reported from C̄, but obtd. from isobutyl bromide or iodide with sodium saccharin in aq. butylcarbitol (1:6517) on refluxing 30 min. (55).]

—— *p*-(Isobutoxy)benzoic acid: m.p. 140–141° u.c. (56). [From C̄ with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (56).] [Note, however, that this prod. does not distinguish C̄ from isoamyl chloride (3:7365) for which the corresp. *p*-(isoamoxy)benzoic acid has m.p. 141–142° (56).]

—— Isobutyl 2,4,6-tri-iodophenyl ether: m.p. 48.0° cor. (52). [This prod. has been obt. from isobutyl bromide (but not C̄) with 2,4,6-tri-iodophenol in alc. NaOEt (52).] [Note that it would not distinguish C̄ from 1-chloropentane (3:7460) or 1-chlorohexane (3:7955).]

—— Isobutyl α-naphthyl ether: b.p. 301.5° cor. (54). (Corresp. picrate, m.p. 104.5–105.5° cor. (54).)

—— Isobutyl β-naphthyl ether: b.p. 204.5° cor. (54), m.p. 33.0–33.5° cor. (54). (Corresp. picrate, m.p. 84.0–85.0° cor. (54).)

3:7135 (1) Timmermans, Martin, *J. chim. phys* **23**, 778–779 (1926). (2) Timmermans, *Bull. soc. chim. Belg.* **27**, 334–343 (1913); *Cent.* **1914**, I 618. (3) Michael, Zeidler, *Ann.* **393**, 110–111 (1912). (4) Linnemann, *Ann.* **162**, 16–17 (1872). (5) Vogel, *J. Chem. Soc.* **1943**, 638–639. (6) Turkevich, Smyth, *J. Am. Chem. Soc.* **64**, 737 (1942). (7) Turkevich, Smyth, *J. Am. Chem. Soc.* **62**, 217 (1940). (8) Wiswall, Smyth, *J. Chem. Phys.* **9**, 357 (1941). (9) Fühner, *Ber.* **57**, 514 (1924). (10) Britton, Coleman, Warren (to Dow Chem. Co.), U.S. 1,984,725, Dec. 18, 1934; *Cent.* **1935**, I 3199.

(11) Lecat, "L'azeotropisme," Brussels, 1918. (12) Lecat, *Rec. trav. chim.* **45**, 624 (1926). (13) Lecat, *Rec. trav. chim.* **46**, 242 (1927). (14) Lecat, *Ann. soc. sci. Bruxelles* **47**, I 152, 155 (1927). (15) Haack (to Chem. Fabrik von Heyden), Ger. 621,693, Jan. 30, 1936; *Cent.* **1936**,

I 3575; *C.A.* **30,** 4876 (1936). (16) Ricard, Allenet et Cie, Brit. 191,002, Feb. 14, 1923; French 545,290, Oct. 9, 1922; Ger. 430,682, June 30, 1926; *Cent.* **1923,** II 907. (17) Sabatier, Mailhe, *Compt. rend.* **169,** 124 (1919). (18) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23,** III 77–89 (1929). (19) Norris, Taylor, *J. Am. Chem. Soc.* **46,** 755–757 (1924). (20) Dehn, Davis, *J. Am. Chem. Soc.* **29,** 1328–1334 (1907).

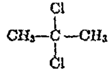
(21) Shoesmith, Mackie, *J. Chem. Soc.* **1928,** 2336. (22) Freund, *J. prakt. Chem.* (2) **1**[illegible], 29–33 (1875). (23) Mouneyrat, *Ann. chim.* (7) **20,** 530 (1900). (24) Pi[illegible] 275–278 (1872). (25) Britton, Coleman, Hadler (to D[illegible] 1934; *Cent.* **1934,** II 3180, *C.A.* **2**[illegible] *C.A.* **30,** 106 (1936). (26) Ha[illegible] Britton, Rousch (to Dow Che[illegible] 1937, I 5045. (28) Ssolonina, *J. Russ. Phys.-Chem*[illegible] *Cent.* **1898,** II 887. (29) Ssolonina, *J. Russ. Phys.-Chem. Soc.* **30,** 8[illegible]–826 (1898); *Cent.* **1899,** I 254. (30) Gault, Beloff, *Bull. soc. chim.* (5) **5,** 295–300 (1938).

(31) Nef, *Ann.* **316,** 21–23 (1901). (32) Senderens, *Bull. soc. chim.* (4) **3,** 827–828 (1908); *Compt. rend.* **146,** 1213 (1908). (33) Sabatier, Mailhe, *Compt. rend.* **141,** 238 (1905). (34) Senderens, *Compt. rend* **200,** 612–615 (1935). (35) Mailhe, *Cent.* **1921,** III 467. (36) Sabatier, Mailhe, *Compt. rend.* **156,** 658 (1913), **138,** 407 (1904). (37) Nutting, Britton, Huscher, Petrie (to Dow Chem. Co.), U.S. 1,993,719, March 5, 1935; *Cent.* **1935,** II 2879–2880; *C.A.* **29,** 2519 (1935). (38) Kistiakowsky, Stauffer, *J. Am Chem. Soc.* **59,** 165–170 (1937). (39) Hass, McBee (to Purdue Research Foundation), U.S. 2,147,577, Feb. 14, 1939; *Cent.* **1939,** II 220; Can. 378,829, Jan. 10, 1939; *Cent.* **1939,** I 3454; *C.A.* **33,** 2151 (1939). (40) Herzfelder, *Ber.* **26,** 1260 (1893).

(41) Britton, Coleman, Moore (to Dow Chem. Co.), U.S. 2,067,473, Jan. 12, 1937; *Cent.* **1937,** II 1894; *C.A.* **31,** 1432 (1937). (42) Olivier, Berger, *Rec. trav. chim.* **41,** 610 (1921). (43) Chablay, *Ann. chim.* (9) **1,** 484, 496 (1914). (44) Konowalow, *J. Russ. Phys.-Chem. Soc.* **27,** 457 (1895); *Bull. soc. chim.* (3) **16,** 865 (1896). (45) Boedtker, *Bull soc. chim.* (3) **31,** 966–968 (1904). (46) Schramm, *Monatsh.* **9,** 615–618 (1888). (47) Coleman, Moore (to Dow Chem. Co.), U.S. 2,207,611, July 9, 1940; *C.A.* **34,** 7934 (1940). (48) Houben, Boedler, Fischer, *Ber.* **69,** 1781 (1936). (49) Fournier, *Bull. soc. chim* (4) **5,** 924 (1909). (50) Underwood, Gale, *J. Am. Chem. Soc.* **56,** 2117–2120 (1934).

(51) Brown, Campbell, *J. Chem. Soc.* **1937,** 1700. (52) Drew, Sturtevant, *J. Am. Chem. Soc.* **61,** 2666 (1939). (53) Neumann, *Ber.* **23,** 999 (1890). (54) V. H. Dermer, O. C. Dermer, *J. Org. Chem.* **3,** 290–291 (1938/39). (55) Merritt, Levey, Cutter, *J. Am. Chem. Soc.* **61,** 15–16 (1939). (56) Lauer, Sanders, Leekley, Ungnade, *J. Am. Chem. Soc.* **61,** 3050 (1939). (57) Gillespie, *J. Am. Chem. Soc.* **56,** 2740–2741 (1934).

3:7140 2,2-DICHLOROPROPANE (Isopropylidene (di)chloride; "acetone (di)chloride")



$C_3H_6Cl_2$ **Beil. I - 105** I_1-(34) I_2-(73)

B.P.			F.P.	
70.5°	at 760 mm.	(1)	**−34.6°** (8) (9)	D_4^{25} = **1.084591** (1)
69.8°		(2)	**−34.4°** (1)	D_4^{20} = **1.09151** (1)
69.7°		(3)	**−33.8°** (5)	
69.69° cor.	at 760 mm.	(4)		n_D^{20} = **1.41167** (1)
69.3°		(5)		
68.9–69.3°		(5a)		D_4^{15} = **1.09843** (1)
68.86–69.06°		(6)		
68.85–68.87°	at 746 mm.	(7)		

C̄ with MeOH (b.p. 64.7°) forms a const.-boilg. mixt., b.p. 55.5°, contg. 79% C̄; C̄ with EtOH (b.p. 78.3°) forms a const.-boilg. mixt., b.p. 63.2°, contg. 85.5% C̄ (2).

[For f.p./compn. data on mixts. of C̄ with methylene (di)chloride (3:5020), with 1,1-dichloroethane (ethylidene (di)chloride) (3:5035), with CCl_4 (3:5100), or with 1,1,1-trichloroethane (methylchloroform) (3:5085) see (8).]

[For prepn. of C̄ from acetone (1:5400) with PCl_5 [55% yield (10) (together with 45%

2-chloropropene-1 (3:7020)) (10)] see (10) (5) (11) (12); for formn. (25.5% (13)) (together with other products) from propane by vapor-phase chlorination at 400° see (13) (14).]

C̃ on hydrolysis by htg. with 8 vols. aq. in s t. at 160–180° (4), or with HI at 130° (4), or on passing with steam over cat. at 550–850° (15) yields acetone (1:5400). [For behavior of C̃ with boilg. aq. + trace of $NaHCO_3$ or with boilg. aq. + Fe see (13).]

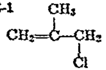
C̃ with alc. KOH yields (12) (13) (16) (17) 2-chloropropene-1 (3:7020), b.p. 22.3° [C̃ with excess alc. KOH yields (18) propyne-1 (allylene), b.p. −27.5°].

C̃ with H_2 over Ni at 300° (19) or over $BaCl_2$ at 380–400° [Beil. I_2-(73)] gives 2-chloropropene-1 (3:7020), b.p. 22.5°.

3:7140 (1) Timmermans, Delcourt, *J. chim. phys.* **31**, 91–92 (1934). (2) Lecat, *Rec. trav. chim.* **46**, 242 (1927). (3) Hass, McBee, Weber, *Ind. Eng Chem.* **28**, 338 (1936). (4) Linnemann, *Ann.* **161**, 67 (1872). (5) Turkevich, Smyth, *J. Am Chem. Soc.* **62**, 2469 (1940). (5a) Kohlrausch, Köppl, *Monatsh.* **65**, 196 (1935). (6) Gross, *Physik. Z* **32**, 589 (1931). (7) Maryott, Hobbs, Gross, *J. Am. Chem. Soc* **63**, 660 (1941). (8) van de Vloed, *Bull. soc. chim. Belg.* **48**, 260, 262 (1939). (9) Timmermans, *Bull. soc. chim Belg* **25**, 300–327 (1911), *Cent.* **1911**, II 1015. (10) *Henne, Renoll, J. Am. Chem. Soc* **59**, 2435 (1937).

(11) Friedel, Ladenburg, *Ann.* **142**, 315–316 (1867). (12) Friedel, *Ann* **112**, 236 (1859). (13) McBee, Hass, Chao, Welch, Thomas, *Ind Eng Chem.* **33**, 176–177 (1941). (14) Hass, McBee (to Purdue Research Foundation), U.S. 2,004,073, June 4, 1935, *Cent.* **1936**, I 1500. (15) Lloyd, Kennedy, U.S. 1,849,844, March 15, 1932, *Cent* **1932**, I 2994. (16) Kahovec, Kohlrausch, *Z. physik. Chem.* **B-46**, 178 (1940). (17) West, Farnsworth, *Trans Faraday Soc.* **27**, 147 (1931). (18) Friedel, *Ann.* **134**, 262–264 (1865). (19) Mailhe, *Bull soc. chim.* (4) **29**, 538 (1921).

3:7145 3-CHLORO-2-METHYLPROPENE-1 (Methallyl chloride; isobutenyl chloride; β-methylallyl chloride; γ-chloroisobutylene)



C_4H_7Cl Beil. I - 209, I_1—, I_2—

B.P. [73.74°	(1)]	$D_4^{20} = 0.9475$ (7)	$n_D^{20} = 1.4340$ (7)
71–74°	(2)		
72.2°	(3) (8)		
71.5–72.5°	(4) (5)		
70–71° (6) at 739 mm.	(7)		

[*See also* 1-*chloro-2-methylpropene*-1 (3:7120).]

Note that for C̃ the designation methallyl chloride is now preferred (3); great care should be used to avoid confusion of C̃ with the isomeric and very closely related 1-chloro-2-methylpropene-1 = isocrotyl chloride = β,β-dimethylvinyl chloride = α-chloroisobutylene (3:7120); both these compounds are now commercial products in the U.S.A.

Commercial C̃ contains approx. 4% (10) of the isomeric β,β-dimethylvinyl chloride (3:7120); owing to the proximity of their boiling points the two isomers are extremely difficult to separate by distillation (8), but owing to the great reactivity of the halogen of C̃ (see amplification below) and the relative unreactivity of the halogen of β,β-dimethylvinyl chloride (3:7120) interference from the latter in *metathetical* reactions of comml. C̃ need not be expected.

[For prepn. of C̃ from 2-methylpropene-1 (isobutylene) with Cl_2 see (3) (2) (5) (9) (other prods. are also formed); for formn. of C̃ as its equilibrium mixt. (10% C̃) with β,β-dimethylvinyl chloride (3:7120) by actn. of H_2SO_4 on latter see (8).]

[For use of C̃ as insecticide see (11) (12); for toxicity studies on beetles see (13); for detn. of C̃ (when used as industrial fumigant) by reaction with ethanolamine in dioxane

(14) or by thermal decomposition (15) see indic. refs.; for use of $\bar{C}$ *in prepn. of cellulose* ethers see (16) (17).]

Reactions involving further substitution of H atoms in $\bar{C}$. [$\bar{C}$ with Cl_2 at room temp. (8) cf. (5) (9) or in pres. of $NaHCO_3$ soln. at 0° (2) gives (70% yield (8)) a mixt. of approximately equal amounts of 1,3-dichloro-2-methylpropene-1 (3:5590) and 1-chloro-2-(chloromethyl)propene-2 (3:5633) (see also next paragraph).]

Reactions involving the double bond of $\bar{C}$. [$\bar{C}$ with Cl_2 (5) (42) or with SO_2Cl_2 (42) also (see above) adds halogen to the unsaturated linkage yielding (5) (42) 1,2,3-trichloro-2-methylpropane (3:5710), b.p. 163.5–164° at 772 mm. (5).]

[$\bar{C}$ with Br_2, however, gives chiefly (93% yield (8)) cf. (5) (9) the expected addition prod., 1-chloro-2,3-dibromo-2-methylpropane [Beil. I-128], b.p. 57° at 5 mm., $D_4^{20} = 1.9168$, $n_D^{20} = 1.5834$ (8).]

[*$\bar{C}$ adds HCl with considerable difficulty*; e.g., $\bar{C}$ with equal vol. 12 *N* HCl at 3°, or $\bar{C}$ at b.p. treated with HCl gas for 2 hrs., shows no reaction (3); however, $\bar{C}$ with equal vol. 12 *N* HCl shaken for 1½ hrs. at 63° forms 30% of the expected 1,2-dichloro-2-methylpropane (3:7430). — $\bar{C}$ with dry HBr gas readily reacts giving (97% yield (8)) 1-chloro-3-bromo-2-methylpropane, b.p. 49° at 15 mm., $D_4^{20} = 1.4839$, $n_D^{20} = 1.4816$ (8) (note that this "abnormal" mode of addition of HBr *is presumably attributable to the presence in* $\bar{C}$ of peroxidic material (8)).]

[$\bar{C}$ with aq. HOCl below 5° (1) (7) cf. (8), or $\bar{C}$ with Cl_2/aq. (8) (18) or even org. hypochlorites (18), gives by addn. of HOCl to unsatd. linkage 1,3-dichloro-2-methylpropanol-2 (3:5977). — $\bar{C}$ with aq. HOBr (from Br_2/KBr in aq.) at room temp. for 4 hrs. gives 97.5% yield (1)) 1-bromo-3-chloro-2-methylpropanol-2, b.p. 84–85° at 20 mm., $D_{20}^{20} = 1.7578$, $n_D^{20} = 1.5171$ (1). — $\bar{C}$ in ether with aq. HgO + I_2 (HOI) at room temp. for 5–6 hrs. gives *(15% yield (1)) 3-chloro-1-iodo-2-methylpropanol-2, b.p. 101–103° at 18 mm.,* n_D^{20} = 1.547 (1).]

[$\bar{C}$ can also add hypochlorite esters; e.g., $\bar{C}$ with *ter*-BuOCl (3:7165) in MeOH + trace *p*-toluenesulfonic acid at 40° for 3–4 hrs. gives (35% yield (6)) *β,β*-dichloro-*ter*-butyl methyl ether (1,3-dichloro-2-methoxy-2-methylpropane), b.p. 170° at 748 mm., $D_{-}^{20} = 1.1953$, $n_D^{20} = 1.4595$ (6).]

[$\bar{C}$ can also undergo cat. hydration of the double bond; e.g., $\bar{C}$, although but slightly sol. in 80% H_2SO_4 at 0°, grad. dissolves on stirring; and after *the solution is poured onto ice* and the liquid distilled (8) (19) 63% of the original $\bar{C}$ can be recovered as *β*-chloro-*ter*-butyl alcohol *(isobutylene chlorohydrin) (1-chloro-2-methylpropanol-2) (3:7752).* Note that other acids can also be used for this hydration, e.g., 85% H_3PO_4, 70% HNO_3, 60% $HClO_4$, benzenesulfonic acid, etc., each having its own optimum conditions (8). Note also that in this reaction some 32% of the initial $\bar{C}$ is not hydrated but is partially isomerized to a mixt. contg. 10% $\bar{C}$ with 90% *β,β*-dimethylvinyl chloride (3:7120) (see also below) (8).]

[$\bar{C}$ can also be rearranged to the isomeric isocrotyl chloride; e.g., $\bar{C}$ (10 moles) with 80% H_2SO_4 (1 mole) stirred at 40° for 2½ hrs. gives an upper phase which conts. abt. 87% isocrotyl chloride + 7% $\bar{C}$ + 6% dichlorides and polymers; after washing free from acid, drying, and distilling it yields 85% *β,β*-dimethylvinyl chloride (3:7120) (8) (20).]

[$\bar{C}$ on sulfonation with dioxane sulfotrioxide in ethylene dichloride gives (21) a complex mixt. of prods.; about 40% of the SO_3 *adds* to the unsatd. linkage giving a cyclic anhydride of the carbyl sulfate type, the remainder *substituting* to yield the three *isomeric mono*sulfonic acids of $\bar{C}$; neither polymerization nor disulfonation takes place; for details the original paper (21) should be consulted.]

[For polymerization of $\bar{C}$ in the pres. of peroxides see (22).]

[$\bar{C}$ condensed with C_6H_6 in pres. of anhydrous liq. HF at 0–10° for 20 hrs. as directed

gives (58% yield on CuCN (10)) (27) methallyl cyanide, b.p. 136.2–136.4°, $D_4^{20} = 0.844$, $n_D^{20} = 1.4202$ (10); note that use of NaCN gives a prod. of somewhat higher b.p., 138.0–139.5° (10), indicating pres. (by rearr.) of some *β,β-dimethylacrylonitrile, b.p. 140–142°.*]

[C̄ (1 mole) with conc. aq. NH_4OH (10 moles) at 90° under press. reacts completely within 2 minutes giving (10) (32) mixt. of 56% methallylamine, b.p. 78.8°, $D_4^{20} = 0.782$, $n_D^{20} = 1.431$ (10) (B̄.HCl, m.p. 190–191° cor. (41); B̄.PkOH, m.p. 202–206° cor. (41)) + 26% di-(methallyl)amine, b.p. 148–149°, $D_4^{20} = 0.799$, $n_D^{20} = 1.446$ (10), + 8% tri-(methallyl)amine, b.p. 194–195° (32), 83–85° at 15 mm., $D_4^{20} = 0.8256$, $n_D^{20} = 1.457$ (10), together with 5% tetra(methallyl)ammonium chloride; C̄ htd. with primary amines behaves in analogous fashion (10) (32).]

[C̄ with Mg in dry ether under very carefully regulated conditions (using large excess of Mg + ether and slow addn. of C̄) gives as high as 90% yield (10) corresp. methallyl MgCl; this with acetaldehyde (1:0100) gives (65% yield (10)) the expected secondary alc. 4-methylpenten-4-ol-2, b.p. 129° (10); similarly C̄ with Mg + acetone (1:5400) in dry ether gives (59 mole % yield (10)) 2,4-dimethylpentene-4-ol-2, b.p. 126° (10) accompanied by (37 mole % yield (10)) of the coupling prod. di-methallyl (see next paragraph); note that this coupling reaction is very difficult to suppress.]

[C̄ with Mg in dry ether (10) (33), or with Na in dry ether (34), gives (yields: 90 mole % (10), 65% (33)) di-methallyl (2,5-dimethylhexadiene-1,5) [Beil. I-259, I_1-(122), I_2-(237)], b.p. 114.3° at 760 mm. (10) (33), $D_4^{20} = 0.7487$ (10), 0.7423 (33), $n_D^{20} = 1.4293$ (33). — Coupling of C̄ with other reactive alkenyl chlorides can also be effected: e.g., C̄ with allyl chloride (3:7035) + Mg in dry ether gives (33) 47% yield 2-methylhexadiene-1,5 [Beil. I-257, I_1-(120)], b.p. 88.1° at 760 mm., $D_D^{20} = 0.7198$, $n_D^{20} = 1.4184$ (33), + 30% di-methallyl (see above) + 12% hexadiene-1,5 (biallyl) (1:8045). — For analogous mixed couplings with 2-chloropentene-3 (piperylene hydrochloride) (3:7400) and with 4-chloro-2-methylbutene-2 (isoprene hydrochloride) (3:7465) see (36).]

[C̄ with $NaNH_2$ in liq. NH_3 gives (27% yield (35)) 2,5-dimethylhexatriene-1,3,5, b.p. 145° at 747 mm., 90.2° at 200 mm., m.p. −9°, $n_D^{21} = 1.5150$ (35); note that an intermediate *x*-chloro-2,5-dimethylhexadiene, b.p. 33–34° at 5 mm., $n_D^{20} = 1.4612$, has been detected (35).]

[C̄ reacts normally with other RMgX compounds: e.g., C̄ with MeMgBr in di-isopropyl ether (ord. ether boils too close to prod.) gives (10) 2-methylbutene-1 (1:8210); C̄ with *n*-BuMgCl gives (83 mole % yield (10)) (33) 2-methylheptene-1, b.p. 119.3° at 760 mm., $D_4^{20} = 0.7206$, $n_D^{20} = 1.4123$ (33) (contaminated with 2-methylheptene-2 formed by rearr. of the former by the inevitable $MgCl_2$ (33)); C̄ with iso-AmMgCl gives (10) 2,6-dimethylheptene-1, b.p. 140–143° (10); C̄ with C_6H_5MgBr gives (10) methallylbenzene (2-methyl-1-phenylpropene-1), b.p. 175–176° (10).]

[For reactn. of C̄ with diethyl malonate (1:3581) and with various diethyl alkylmalonates see (37); for prepn. of methallyl substituted barbituric acids (37) (4) or thiobarbituric acids (38) see indic. refs.]

—— Methallyl acetate [Beil. I-137, I_2-(150)]: b.p. 124° at 760 mm., $D_{20}^{20} = 0.9239$, $n_D^{20} = 1.4129$ (39). [From C̄ + KOAc at 150° in s.t. (5) (9) cf. (10).] [For data on the formate, propionate, and *n*-butyrate see (39).]

—— Methallyl benzoate: yel. odorless oil, b.p. 120° at 50 mm. (40). [Prepd. indirectly (40).]

—— Methallyl *p*-nitrobenzoate: unreported.

—— Methallyl 3,5-dinitrobenzoate: unreported.

Ⓓ *N*-(Methallyl)phthalimide: white cryst. from MeOH, m.p. 88.5–90° cor. (41). [From C̄ + K phthalimide in s.t. at 150° for 3 hrs. (41).]

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(10) Tamele, Ott, Marple, Hearne, *Ind. Eng. Chem.* **33**, 115–120 (1941).
(11) Hymas, *Food* **9**, 254–257 (1940); *C.A.* **35**, 4105 (1941) (12) Briejer, *Nature* **141**, 1099–1100 (1938). (13) Richardson, Casanges, *J. Econ. Entomol.* **35**, 664–668 (1942); *C.A.* **37**, 687 (1943). (14) Winteringham, *J. Soc. Chem. Ind.* **61-T**, 186–187 (1942); *C.A.* **37**, 1951 (1943). [illegible] **37**, 1951 (1943). (16) Hahn [illegible] (17) Maxwell (to du Pont [illegible] (to Shell Development Co.), [illegible] sche Petroleum Matschappij, Brit. 435,096, Oct. 10, 1935; French 789,289, Oct. 25, 1935, *Cent.* **1936**, II 865. (19) Groll, Burgin (to Shell Development Co.), U.S. 2,042,222, May 26, 1936, *Cent.* **1937**, I 1546; *C.A.* **30**, [illegible] 791,644, Dec. 14, 1935; *Cent.* [illegible] J.S. 2,042,223, May 26, 1936; [illegible]
(21) Suter, Bordwell, *J. Am. Chem. Soc.* **65**, 507–517 (1943) (22) Bauer, Götz (to Röhm & [illegible] Weinmayr, [illegible] U.S. 2,072,- [illegible] Bataafsche [illegible] ,25) Hearne, Tamele, Converse, *Ind. Eng. Chem.* **33**, 805–809 (1941) (26) Groll, Ott (to Shell Development Co.), U.S. 2,042,219, May 26, 1936, *Cent.* **1937**, I 1013, *C.A.* **30**, 4871 (1936). (27) Groll, Ott (to Shell Development Co.), U.S. 2,097,155, Oct. 26, 1938; *Cent.* **1939**, I 1652, *C.A.* **32**, 194 (1938). (28) Backer, Kramer, *Rec. trav. chim.* **53**, 1102 (1934). (29) Williams (to Shell Development Co.), U.S. 2,043,941, June 9, 1936, *C.A.* **30**, 5336 (1936)· Can. 353,986, Nov. 5, 1935, *C.A.* **30**, 1472 (1936). (30) Bruson, Eastes, *J. Am. Chem. Soc.* **59**, 2012 (1937)
(31) Merejkowsky, *Bull. soc. chim.* (4) **37**, 711–713 (1925) (32) Tamele, Groll (to Shell Development Co.), U.S. 2,172,822, Sept. 12, 1939; *Cent.* **1939**, II 4350, *C.A.* **34**, 448 (1940). (33) Henne, Chanan, Turk, *J. Am. Chem. Soc.* **63**, 3475 (1941). (34) Przybytek, *Ber.* **20**, 3240–3241 (1887). (35) Kharasch, Nudenberg, Sternfeld, *J. Am. Chem. Soc.* **62**, 2035 (1940). (36) Henne, Gilman, *J. Am. Chem. Soc.* **66**, 392–394 (1944) (37) Doran, Shonle, *J. Am. Chem. Soc.* **59**, 1625–1626 (1937) (38) Tabern, Volweiler, *J. Am. Chem. Soc.* **57**, 1961–1963 (1935). (39) Ryan, Shaw, *J. Am. Chem. Soc.* **62**, 3469 (1940) (40) Kleinfeller, *Ber.* **62**, 1597 (1929).
(41) Adams, Cairns, *J. Am. Chem. Soc.* **61**, 2466 (1939). (42) Mooradian, Cloke, *J. Am. Chem. Soc.* **68**, 787 (1946). (43) Köhler (to Röhm & Haas Co.) U.S. 2,323,781, July 6, 1943; *C.A.* **38**, 116 (1944).

3:7150 α-CHLOROETHYL METHYL ETHER C_3H_7OCl Beil. I - 606
(α-Methoxyethyl chloride) I_1-(327)
I_2-(674)

$$CH_3\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}.O\,CH_3$$

B.P.

72–73° cor. at 751 mm. (1)	D_4^{20} = **0.9909 (2)**	n_D^{20} = **1.4004 (1)**
70–72° at 746 mm. (2)	**0.9902 (1)**	**1.3969 (2)**

[For prepn. (yields: 97% (1), 95% (2)) from paraldehyde (1:0170) + methyl alc. (1:6120) + dry HCl see (1) (2) (3).]

$\bar{C}$ on stdg. polymerizes to dark tarry residue.

[$\bar{C}$ with Br_2 at 0° gives (3) α,β-dibromoethyl methyl ether, b.p. 67–69° at 22 mm. (3).]

$\bar{C}$ on shaking with aq. yields acetaldehyde (1:0100), methyl alc. (1:6120), + HCl.

3:7150 (1) Henze, Murchison, *J. Am. Chem. Soc.* **53**, 4077–4079 (1931). (2) Wallace, Henze, *J. Am. Chem. Soc.* **64**, 2882 (1942). (3) Baker, *J. Chem. Soc.* **1942**, 522.

3:7151 4-CHLOROBUTENE-1 $CH_2—CH_2—CH=CH_2$ (with Cl on first C) C_4H_7Cl Beil. S.N. 11

B.P. 75.0° at 773 mm. (1) $D_4^{20} = 0.9211$ (1) $n_D^{20} = 1.42330$ (1)

Colorless liq. with odor similar to allyl chloride but less strong; insol. aq.

[For prepn. of Č from buten-1-ol-4 (allylcarbinol) [Beil. I-441, I_1-(226), I_2-(480)] with PCl_3 + pyridine (41% yield) see (1).] [Č is not formed (2) (3) during reactn. of butadiene-1,3 with HCl.]

3:7151 (1) Juvala, *Ber.* **63**, 1993 (1930). (2) Kharasch, Kritchevsky, Mayo, *J. Org. Chem.* **2**, 494 (1938). (3) Ganguly, *J. Indian Chem. Soc.* **13**, 581, 684 (1936).

3:7153 ACRYLOYL CHLORIDE (Propenoyl chloride) $CH_2=CH—C=O$ (with Cl on C) C_3H_3OCl Beil. II - 400, II_1—, II_2-(388)

B.P. 75–76°	(1)	$D_4^{20} = 1.1136$ (13)	$n_D^{20} = 1.4343$ (13)
74–75°	(11)		
74–76° at 760 mm.	(13)	$D^0 = 1.14$ (1)	
30–32° at 140 mm.	(13)		

Colorless mobile strongly lachrymatory liq., fumg. in air.

[For prepn. of Č from sodium acrylate with $POCl_3$ (yields 80% (11), 60% (1), 27% (12), 22% (9) (2) (3) (4), with $SOCl_2$ (19% yield (9)), or from β-chloropropionyl chloride (3:5690) by loss of HCl (35% yield (12)) when passed over suitable cat. at 280–300° (5) see indic. refs.; for prepn. of Č from acrylic acid (1:1020) with PCl_3 (66% yield) see (13).]

[For polymerization of Č by light (10) in pres. of a small amt. of org. base see (6); for polymerization of Č in pres. of u.v. light or by dibenzoyl peroxide see (9).]

[Č with MeOH yields (1) methyl β-chloropropionate (3:5765), b.p. 148°; Č with EtOH yields (1) ethyl β-chloropropionate (3:8290), b.p. 162°; Č with phenol yields (1) phenyl β-chloropropionate, b.p. 154–157° at 30 mm. (1); note, however, that Č reacting with a large excess of alcs. or phenols and/or in the pres. of acid binding agents such as $CaCO_3$ yields (7) esters of acrylic acid.]

[Č with Na acrylate yields (1) acrylic anhydride, b.p. 97° at 35 mm. (1).]

Č with C_6H_6 + $AlCl_3$ yields (8) (2) (by Friedel-Crafts reactn. and subsequent ring closure) indanone-1 (1:5144), m.p. 42°.

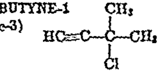
Č in $CHCl_3$ treated with Br_2 in $CHCl_3$ yields (1) 2,3-dibromopropionyl chloride, b.p. 191–193°, 97–99° at 37 mm. (1), $D^0 = 2.181$ (1), which with warm aq. easily hydrolyzes to α,β-dibromopropionic acid, m.p. 64° (1).

Č on hydrolysis yields (1) acrylic acid (1:1020) q.v. (for the amide, m.p. 84–85° (11), anilide, and p-toluidide corresp. to Č see 1:1020).

3:7153 (1) Moureu, *Ann. chim.* (7) **2**, 161–174 (1894). (2) Kohler, *Am. Chem. J.* **42**, 380 (1909). (3) van der Burg, *Rec. trav. chim.* **41**, 23 (1921). (4) Gilman, Heckert, McCracken, *J. Am. Chem. Soc.* **50**, 438 (1928). (5) I. G., Brit. 333,079, Aug. 28, 1930; *Cent.* **1930**, II 2830; U.S. 2,050,752, Aug. 11, 1936; *C.A.* **30**, 6762 (1936). (6) Fikenscher (to I. G.), Ger. 577,040, May 22, 1933; *Cent.* **1933**, II 1250; *C.A.* **27**, 3950 (1933). (7) Bauer, Lauth (to Röhm & Haas Co.), Ger. 570,955, Feb. 22, 1933; *Cent.* **1933**, I 2608. (8) Ref. 1, pp. 198–202. (9) Marvel, Levesque, *J. Am. Chem. Soc.* **61**, 3244–3246 (1939). (10) Staudinger, Urech, *Helv. Chim. Acta* **12**, 1131 (1929).

(11) Jones, Zomlefer, Hawkins, *J. Org. Chem.* **9**, 500–507 (1944). (12) Mowry, *J. Am. Chem. Soc.* **66**, 371–372 (1944). (13) Rehberg, Dixon, Fisher, *J. Am. Chem. Soc.* **67**, 209 (1945).

3:7155 3-CHLORO-3-METHYLBUTYNE-1 (2-Chloro-2-methylbutyne-3)



C_5H_7Cl Beil. S.N. 12

B.P. 76° (1)
74–76° (2)

$D_{?}^{?} = 0.9061$ (1)

[For prepn. of $\bar{C}$ from 2-methylbutyn-3-ol-2 (dimethyl-ethynyl-carbinol) on shaking as specified (1) (3) with HCl + $CuCl_2$ + NH_4Cl; if Cu_2Cl_2 is used or if reactn. is protracted $\bar{C}$ is isomerized (cf. (4)) to 1-chloro-3-methylbutadiene-1,2 (3:7390) q.v.; for reverse conversion of latter to $\bar{C}$ (and other products) by htg. with $CaCO_3$ + aq. see (3).]

$\bar{C}$ on htg. with aq. + $CaCO_3$ at 80° gives (2) the precursor 2-methylbutyn-3-ol-2.

$\bar{C}$ with $NH_4OH/AgNO_3$ gives (1) a white ppt. [dif. from 1-chloro-3-methylbutadiene-1,3 (3:9200)].

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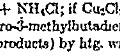
3:7160 1-CHLOROBUTANE (*n*-Butyl chloride; *n*-propylcarbinyl chloride)



C_4H_9Cl Beil. I - 118
I_1-(38)
I_2-(80)

B.P.		F.P.		
78.6° at 760 mm.	(1)	−123.1° (1)	D_4^{25} = 0.88098 (2)	
78.50° at 760 mm.	(2)	(2)		
78.3–78.4° at 760 mm.	(3)		D_4^{20} = 0.8866 (8)	
78.05° at 760 mm.	(4)		0.88648 (2)	
78.4–78.7° u.c.	(5)		0.8859 (8)	
78.4–78.6°	(6)		0.8845 (12)	
78.1° at 760 mm.	(7)		0.88387 (11)	
78.0° at 762 mm.	(8)		(19)	
78°	(9)			
77.96° cor.	(10)		D_4^{15} = 0.89197 (2)	
77.7–77.9° at 762.7 mm.	(11)		0.88923 (11)	
77.6–77.7° at 743 mm.	(3)		(19)	
77.6° at 748 mm.	(12)			n_D^{20} = 1.4023 (9) (6)
77.6° at 741.3 mm.	(13)			1.40223 (8)
77.5–77.9° at 760 mm.	(14)			1.4021 (18)
77.5°	(15) (16)			1.40173 (17)
77.3–77.6°	(17)			1.40150 (8)
77.0° at 769 mm.	(8)			1.40148 (16)
76–77° at 750 mm.	(18)			1.40147 (19)

See also Note 1.

Note 1: For further data on b.p. at press. over range 565–760 mm. see (15).

Note 2: $\bar{C}$ is very spar. sol. aq.; e.g., 0.066 wt. % at 12° (20).

Binary systems of $\bar{C}$ with other org. cpds. For f.p./compn. data on mixts. of $\bar{C}$ with *ter*-BuCl (3:7045) see (21); for partial vapor press. (17) or n_D^{20} (22) of mixts. of $\bar{C}$ with *n*-heptane (1:8575) or *n*-BuBr see indic. refs.

$\bar{C}$ *forms azeotropes with various other org. cpds.; e.g.,* $\bar{C}$ with MeOH (1:6120) forms a const.-boilg. mixt., b.p. 57.0° at 760 mm., contg. 73 wt. % $\bar{C}$ (4); $\bar{C}$ with EtOH (1:6130) forms a const.-boilg. mixt., b.p. 65.7° at 760 mm., contg. 79.7 wt. % $\bar{C}$ (4); $\bar{C}$ with *n*-PrOH (1:6150) forms a const.-boilg. mixt., b.p. 74.8° at 760 mm., contg. about 82 wt. % $\bar{C}$ (4); $\bar{C}$ with iso-PrOH (1:6135) forms a const.-boilg. mixt., b.p. 70.8° at 760 mm., contg. 77 wt. % $\bar{C}$ (4); $\bar{C}$ with isobutyl alc. (1:6165) forms a const.-boilg. mixt., b.p. 77.65° at 760 mm., contg. 96 wt. % $\bar{C}$ (4); $\bar{C}$ with EtOAc (1:3015) forms a const.-boilg. mixt., b.p. 75.5° at 760 mm., contg. 55 wt. % $\bar{C}$ (23).

[For prepn. of $\bar{C}$ from *n*-butyl alc. (1:6180) with dry HCl gas on protracted htg. (11) (13) (24) (25), with conc. aq. HCl + $ZnCl_2$ (2 moles) (yields: 76–78% (26) (27) (29), 66–72% (30), 64–66% (28), 65% (8)) (31), other metal salts (31) (32), or H_3PO_4 (33); with PCl_3 + $ZnCl_2$ (60% yield (30)) (34) or PCl_3 + pyridine (for important study of mechanism see (35) (36)); with PCl_5 + $ZnCl_2$ (74% yield (30)) cf. (35) (36); with $SOCl_2$ + pyridine (71% yield (8)) (for important study of mechanism see (37) (36)) see indic. refs.]

[For formn. of $\bar{C}$ from *n*-butyl HSO_4 with HCl (25); from *n*-butyl MgBr with *p*-toluenesulfonyl chloride (8.7% yield (38)); from *n*-butyl *p*-toluenesulfonate as by-prod. of its reactn. with benzyl MgCl in prepn. of *n*-amylbenzene (39) cf. (40) (41); from *n*-butyl iodide with $HgCl_2$ in s.t. at 120–120° for 2 hrs. (10); from *n*-butylamine with HNO_2 (5.2% $\bar{C}$ accompanied by 36.5% butenes + 25% butanol-1 + 13.2% butanol-2 + 2.8% 2-chlorobutane (42)); from *n*-butane with Cl_2 at 400–475° (together with other prods. (3)) see indic. refs.]

[For use as denaturant for alc. see (43) (for detn. of $\bar{C}$ in denatured alc. see (4)); *for use in removal of water from volatile fatty acids see (45); for study of anthelmintic props. see (46).*]

Pyrolysis of $\bar{C}$. [$\bar{C}$ at 450–650° without catalyst loses HCl and yields exclusively butene-1 (3) (47); however, $\bar{C}$ passed at 450° over $CaCl_2$ cat. gives mixt. contg. 20% butene-1 + 80% *cis* + *trans* isomers of butene-2 (3) (47) (for influence of other cat. cf. (48) (49)).]

Further halogenation of $\bar{C}$. [$\bar{C}$ with Cl_2 under various conditions (50) (51) (52) (53) (54) (5) gives a mixt. of 1,1-dichlorobutane (3:7550), 1,2-dichlorobutane (3:7680), 1,3-dichlorobutane (3:7925), and 1,4-dichlorobutane (3:5835) (together with higher chlorination prods.); note that the chlorination is facilitated by peroxides or by light but inhibited by O_2 (e.g., $\bar{C}$ with Cl_2 in absence of air at 0° in dark reacts 7% in 20 hrs. but in pres. of 2 mole % ascaridole 85% *in same time or in light 100% in 1 min.; in pres. of 2%* O_2 *in dark* no reactn. occurs in 96 hrs. (18). — $\bar{C}$ (2.5 moles) with SO_2Cl_2 (1 mole) + trace dibenzoyl peroxide 3 hrs. under reflux in the dark gives (55) mixt. contg. 25% 1,2-dichlorobutane (3:7680) + 50% 1,3-dichlorobutane (3:7925) + 25% 1,4-dichlorobutane (3:5835). — $\bar{C}$ (1 mole) with $SbCl_5$ (1 mole) gives on warming (56) 2,3-dichlorobutane (3:7615).]

$\bar{C}$ with Br_2 in pres. of Fe gives (57) 1,2-dibromobutane [Beil. I-120, I_1-(83)], b.p. 166°.

Reactions of the halogen atom of $\bar{C}$. Note that in $\bar{C}$ the chlorine atom is much less reactive than that of *sec.*-butyl chloride (3:7125) or *ter*-butyl chloride (3:7045).

[For study of hydrolysis of $\bar{C}$ in pres. and abs. of acid see (58).]

[For study of rate of reactn. of $\bar{C}$ with LiI, NaI, or KI in acetone see (59) (60).]

[For study of rate of reactn. of $\bar{C}$ with Na *n*-propylate see (61).]

[$\bar{C}$ with aniline as directed yields (62) *N*-(*n*-butyl)aniline and/or *N,N*-di-(*n*-butyl)aniline; for analogous study of $\bar{C}$ with *N*-methylaniline (63), *N*-ethylaniline (63), *o*-toluidine (64), *p*-toluidine (64), *unsym.-m*-xylidine (65) see indic. refs.]

[$\bar{C}$ with C_6H_6 + $AlCl_3$ gives (69% yield (66)) *sec.*-butylbenzene (1:7490) (note isomerization of carbon chain) (*for comparison of reactivity of* $\bar{C}$ *with other n-butyl halides see (67)*); $\bar{C}$ with C_6H_6 + Al/Hg gives both (68) *sec.*-butylbenzene (1:7490) and *n*-butylbenzene

(1:7515). — $\bar{C}$ with toluene + $AlCl_3$ gives (45% yield (69) of a mixt. of both *m*- and *p*-*sec.*-butyltoluenes.]

[$\bar{C}$ with C_6H_6 in dry liq. HCl at 195° under press. gives (70) 30% yield *sec.*-butylbenzene (1:7490) + 60% di-(*sec.*-butyl)benzene; for analogous behavior of $\bar{C}$ with toluene see (70).]

[$\bar{C}$ with CO + $AlCl_3$ or similar cat. under press. yields (71) acids and ketones.]

Reaction of $\bar{C}$ to form organometallic cpds. [$\bar{C}$ with metallic Li in dry ether under N_2 gives (yields: 75–80% (72), 77% (73), 70–75% (74)) *n*-butyllithium (for study of rate of formn. of *n*-BuLi as compared with *n*-BuBr, C_6H_5Br, C_6H_5I see (85)); this prod. with dry CO_2 *in ether at 0° gives (45% yield (75)) di-n-butyl ketone (1:5493) or with CO_2 in* C_6H_6 at room temp. also (75) tri-*n*-butylcarbinol; for study of relative reactivity of *n*-BuLi as compared with *n*-BuMgBr, C_6H_5MgBr, etc., see (76); note, however, that full chemistry of *n*-BuLi cannot be discussed here.]

[$\bar{C}$ with metallic Na in pet. ether yields (77) *n*-butylsodium; on carbonation with CO_2 this prod. gives (77) (78) (79) (80) both *n*-valeric acid (1:1060) and *n*-propylmalonic acid; for study of reactn. of *n*-BuNa with C_6H_6 see (77); *note, however, that full chemistry of* *n*-BuNa cannot be covered here.]

$\bar{C}$ with Mg in dry ether gives (yields: 98.5% (81), 91.2% (82) (83), 85% (84)) *n*-BuMgCl; for studies on rate of formn. of *n*-BuMgCl (as compared with C_6H_5MgBr, *or with other* *n*-Bu halides, etc.) (85), on effect of rapid addn of $\bar{C}$ on yield (83), on effect of concentration of $\bar{C}$ (84) see indic. refs.; for study of equilibrium composition of ether solns. of *n*-BuMgCl see (86) (87); for study of competitive reaction of mixts. of $\bar{C}$ with *n*-BuBr and with *n*-BuI in formn. of RMgX see (88). — For certain important reactions of *n*-BuMgCl see below but note that full chemistry of this cpd. cannot be included here.

[$\bar{C}$ with Mg + trace of I_2 but *without solvent* at 79–82° for 3 hrs. gives (10% *yield* (89)) *n*-octane (1:8655); $\bar{C}$ + Mg + I_2 in toluene in similar fashion gives (6% yield (89)) *p*-(*n*-butyl)toluene.]

Ⓓ **n-Valeric acid** (1:1060) q.v. [From $\bar{C}$ by conversion to *n*-BuMgCl (see above) and carbonation with CO_2 (yields: 72–73% (90), 80% (91)) (note that this prod. may be accompanied by *more or less di-n-butyl ketone (1:5493) and tri-n-butylcarbinol* (91)), or by conversion of $\bar{C}$ with KCN to *n*-valeronitrile and hydrolysis of the latter with 67% H_2SO_4 (52) (92).]

Ⓓ ***n*-Valeranilide**: m.p. 62–63° u.c. (93), 63° cor. (94). [From $\bar{C}$ by conversion to *n*-BuMgCl (see above) and reactn. in dry ether with phenyl isocyanate (93) (42) cf. (93).]

Ⓓ **n-Valero-*p*-toluidide**: m p. 72–73° u.c. (93). [From $\bar{C}$ by conversion to *n*-BuMgCl *(see above) and reactn. in dry ether with p-tolyl isocyanate* (93).] — [Note that this derivative does not afford good distinction from *n*-amyl chloride (3:7460) for which the corresp. *n*-capro-*p*-toluidide has m.p. 74–75° u.c. (93)]

Ⓓ ***n*-Valero-α-naphthalide**: m p. 109–110° u.c. (93). [From $\bar{C}$ by conversion to *n*-BuMgCl (see above) and reactn. in dry ether with α-naphthyl isocyanate (93).] — [Note that this derivative does *not* afford good distinction from isoamyl chloride (3:7365) *for which the corresp. isocaproic α-naphthalide has m p. 110–111° u c.* (93).]

—— ***n*-Butyl mercuric chloride** (*n*-BuHgCl): m.p. 130° cor. (95), 129° (96), 127.5° (98), 126° (96), 125.5° (97), 125° (99). [Prepd. indirectly but should be easily preparable from *n*-BuMgCl + $HgCl_2$ cf. (98), *since it has been similarly prepd. from n-BuMgBr* (95)]

Ⓓ **S-(*n*-Butyl)isothiourea picrate**: m.p 177° (100). [From $\bar{C}$ (1 g.) with thiourea (1 g.) in alc. (10 ml.) on refluxing for 2 hrs., then adding PkOH (1 g.), htg. until a clear soln. results, then cooling (100).] — [Note that this derivative does not dis-

tinguish $\bar{C}$ from *n*-propyl chloride (3:7040) for which the corresp. *S*-(*n*-propyl)-isothiourea picrate has m.p. 176° (100), nor from isoamyl chloride (3:7365) for which the corresp. *S*-(isoamyl)isothiourea picrate has m.p. 173° (100).]

—— *N*-(*n*-Butyl)phthalimide (1-(*N*-phthalimido)butane): cryst. from dil. AcOH, m.p. 34° (101), b.p. 311.8° cor. at 758 mm. (102). [Prepd. indirectly from *n*-butylamine (101) (102); direct prepn., e.g., from $\bar{C}$ + K phthalimide in pres. of KI never reported and m.p. too low to serve as good derivative.]

Ⓓ *N*-(*n*-Butyl)-3-nitrophthalimide: pr. from CS_2, m.p. 71–72° (103). [From $\bar{C}$ with K 3-nitrophthalimide on refluxing for 10 hrs. (103); for photographs of crystals see (104).]

Ⓓ *N*-(*n*-Butyl)tetrachlorophthalimide: pl. from alc., m.p. 153–154° (105). [From $\bar{C}$ with K tetrachlorophthalimide by htg. at 200° for 10 hrs. (105).]

Ⓓ *N*-(*n*-Butyl)saccharin: cryst. from dil. alc., m.p. 38° (106). [From $\bar{C}$ with sodium saccharin in aq. butylcarbitol (1:6517) contg. KI on refluxing for 30 min. (106).]

—— *N*-(*n*-Butyl)-*N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide: cryst. from 75% alc., m.p. 74.5° u.c. (107). [This prod. has not been reported from $\bar{C}$ but has been obt. from *n*-BuBr with *N*-(*p*-bromobenzenesulfonyl)-*p*-anisidide in alc. KOH after 1 hr. reflux (107).]

—— *p*-(*n*-Butoxy)benzoic acid: m.p. 147–148° (108), changing to a cloudy viscous liq. clearing sharply at 160° (108) cf. (109). [From $\bar{C}$ with ethyl *p*-hydroxybenzoate (1:1534) in abs. alc. NaOEt on refluxing 1 hr. (108)]. — [Note, however, that this prod. does not distinguish $\bar{C}$ from *n*-propyl chloride for which the corresp. *p*-(*n*-propoxy)benzoic acid has m.p. 145.5–147°; the two prods. do, of course, have slightly different Neut. Eqs.]

—— *n*-Butyl 2,4,6-triiodophenyl ether: m.p. 66° cor. (110). [This prod. has not been reported for $\bar{C}$ itself but has been obtd. from *n*-BuBr with 2,4,6-triiodophenol in abs. alc. NaOEt on refluxing for 30 min. (110).]

—— *n*-Butyl α-naphthyl ether: b.p. 308.5° cor. (111), 310° (112) (corresp. picrate, m.p. 88.0° cor., Neut. Eq. 429 (111)).

—— *n*-Butyl β-naphthyl ether: b.p. 309.0° cor. (111), 311° (112); m.p. 33.0–33.5° (111) (corresp. picrate, m.p. 67.0–67.5° cor. (111), 67° (113)).

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3:7165 *ter*-BUTYL HYPOCHLORITE $(CH_3)_3C—OCl$ C_4H_9OCl Beil. I —
(Trimethylcarbinyl hypochlorite) I_1—
I_2-(415)

B.P. 79.6° at 750 mm. (1) $D_4^{18} = 0.9583$ (1)
77–79° (16)

Pale yellow mobile liquid with characteristic irritating odor. — $\bar{C}$ violently attacks the eyes and mucous membranes. — $\bar{C}$ is relatively stable and if protected from bright light can be kept at ordinary temps. for months with little or no decomposition (1). $\bar{C}$ should, however, be handled with care since it is particularly susceptible to photochemical decomposition which may occur with explosive violence (2).

[For prepn. of $\bar{C}$ from *ter*-butyl alcohol (1:6140) + Cl_2 + alk. in pract. quant. yield *see* (1) (2) (3), *60% yield* (16); *from ter-butyl alc.* (1:6140) + HOCl in CCl_4 *see* (15); *for* manufacture of $\bar{C}$ see (4).] [For use in bleaching of textiles, fruits, etc., see (5) (6) (7).]

[For general survey of reactns. of $\bar{C}$ see (8); for study of reactns. of $\bar{C}$ with olefins (2) (13) (16) (17) (18) or olefins contg. activating groups (9) (10), with group $R_2C{=}N.MgX$ (3), *or with Schiff's bases* (11) (12) *see indic. refs.; for study of* $\bar{C}$ *in Friedel-Crafts reactn. see* (14).]

$\bar{C}$ on sufficient htg. or on exposure to bright sunlight yields (1) acetone (1:5400) + methyl chloride (3:7005). — [For data on stability of $\bar{C}$ in aq. or in CCl_4 see (15).]

$\bar{C}$ with aq. KI acidified with AcOH *yields* I_2 (use in detn. of $\bar{C}$ (1)).

3:7165 (1) Chattaway, Backeberg, *J. Chem. Soc.* **123**, 2999–3003 (1923). (2) Irwin, Hennion, *J. Am. Chem. Soc* **63**, 858–860 (1941). (3) Hauser, Humble, Haus, *J. Am. Chem. Soc.* **54**, 2476–2480 (1932). (4) Deanesly, (to Shell Development Co.), U.S. 1,938,175, Dec. 5, 1933; *Cent.* **1934**, I 1709; *C.A.* **28**, 1053 (1934). *(5) Magill (to du Pont), U.S. 2,155,728; April 25,* 1939; *Cent.* **1939**, II 1808; *C.A.* **33**, 6069 (1939). (6) Carlisle (to du Pont), U.S. 2,152,532, March 28, 1939; *Cent.* **1939**, II 276, *C.A.* **33**, 5085 (1939). (7) Imperial Chem. Ind., Brit. 523,467, July 15, 1940; *C.A.* **34**, 6470 (1941). (8) Clark, *Chem. News* **143**, 265–267 (1931). (9) Emling, Vogt, Hennion, *J. Am. Chem. Soc.* **63**, 1624–1625 (1941). (10) Jackson, Pasiut, *J. Am. Chem. Soc.* **49**, *2071–2079 (1927).*

(11) Fuscp, Musante, *Gazz. chim. ital.* **66**, 258–264 (1936); *Cent.* **1936**, II 2341; *C.A.* **31**, 1777 (1937). (12) Musante, Fusco, *Gazz. chim. ital.* **66**, 639–648 (1936); *Cent.* **1937**, I 1674; *C.A.* **31**, 3459 (1937). (13) N. V. de Bataafsche Petroleum Maatschappij, French 740,350, Jan. 24, 1933; *Cent.* **1933**, I 2870; *C.A.* **27**, 2160 (1933). (14) Bergman, Lowy, *J. Am. Chem. Soc.* **60**, 2596–*2597 (1938). (15) Taylor, MacMullin, Gammal, J. Am. Chem. Soc. 47, 397–398 (1925).* (16) Hanby, Rydon, *J. Chem. Soc.* **1946**, 114–115. (17) Harford (to A. D. Little, Inc.), U.S. 2,207,983, July 16, 1940; *C.A.* **34**, 7932 (1940): U.S. 2,107,789, Feb. 8, 1938; *Cent.* **1938**, I 4718; *C.A.* **32**, 2543 (1938): U.S. 2,054,814, Sept. 22, 1936; *Cent.* **1937**, I 1016; *C.A.* **30**, 7584 (1936). (18) Langedijk (to Shell Development Co.) U.S. 2,106,353, Jan. 25, 1938; *C.A.* **32**, 2543 (1938); not in *Cent.*

3:7170 PROPIONYL CHLORIDE $CH_3.CH_2.C{=}O$ C_3H_5OCl Beil. II - 243
　　　　　　　　　　　　　　　　　　　　　|　　　　　　　　　　II_1-(108)
　　　　　　　　　　　　　　　　　　　　Cl　　　　　　　　　　II_2-(223)

B.P.		F.P.				
80°	(1) (2) (3)	−94.0° (9)	$D_4^{25} = 1.0508$	(10)	$n_D^{25} = 1.4057$	(1)
79–80°	(4)					
78.3° at 766 mm.	(5)		$D_{25}^{25} = 1.0409$	(1)		
78.3°	(6)					
77.8–78.3° at 723.7 mm.	(7)		$D_4^{20} = 1.0646$	(7)	$n_D^{20} = 1.4057$	(7)
77–78.5°	(8)		1.0565	(5)	1.4038	(5)

[For prepn. of $\bar{C}$ from propionic acid (1:1025) with PCl_5 (77% yield (11)), with PCl_3 *(yields: 67.5% (12), 61% (13), 46% (14))* (15) (16) *(note that excess* PCl_3 *may not be*

used since its b.p., 76°, is too close to that of $\bar{C}$ for subsequent sepn.), with $PCl_3 + ZnCl_2$ (91% yield (11)), with $SOCl_2$ (4) (note that excess $SOCl_2$ may not be used since its b.p., 79°, is almost identical with that of $\bar{C}$), with benzoyl chloride (3:6240) (yield 84–89% (8)) (17), with sodium chlorosulfonate (18), with benzenesulfonyl chloride + NaCl (18), with $Cl_2 + S_2Cl_2$ in cold (37% yield (19)), with $SiCl_4$ in xylene at 50° (50% yield (20)), or with acetonitrile + HCl gas at 0° (21) see indic. refs., for prepn. of $\bar{C}$ from propionic anhydride (1:1100) with phosgene (3:5000) + cat. as directed see (22).]

[$\bar{C}$ with Cl_2 (67) in CCl_4 in sunlight (15) at 0° (23) or in dark at 40° (24) or $\bar{C}$ with SO_2Cl_2 in CCl_4 in pres. of dibenzoyl peroxide refluxed 4–6 hrs. in dark (25) gives a mixt. contg. mainly β-chloropropionyl chloride (3:5690) accompanied also by α-chloropropionyl chloride (3:5320) yield: 60% β isomer + 40% α isomer (25)), note that in the pres. of I_2 instead of dibenzoyl peroxide only α-chloropropionyl chloride (3:5320) (45% yield (26)) is produced (25).]

[$\bar{C}$ with Br_2 (1 mole) at 80° evolves HCl and gives (100% yield (12)) (27) (28) α-bromopropionyl *bromide* [Beil. II-256, II_1-(230)], *b.p. 153–155° (12); the reaction is accelerated by light, but the photobromination is retarded by* O_2 *(29).*]

[$\bar{C}$ with Na propionate on htg. (14) (30) or $\bar{C}$ with Ag propionate on distn. (31) gives (80% yield (31)) propionic anhydride (1:1100).]

[$\bar{C}$ passed over heated Ni cat. decomposes (32) into ethylene, HCl + CO, accompanied by smaller amts. methane, hydrogen, and CO_2. — $\bar{C}$ with Na in abs. ether is claimed (33) to yield the dipropionate of hexen-3-diol-3,4 [Beil. II-242], b.p. 108–109° at 10 mm. (33).]

[$\bar{C}$ with *ter*-butyl MgBr in dry ether yields (34) not only the expected coupling product *ter*-butyl methyl ketone (pinacolone) (1:5425) but also diethyl ketone (1:5420), propanol-1 (1:6150), and propionic acid (1:1025) accompanied by the propionates of *ter*-butyl-ethyl-carbinol (2,2-dimethylpentanol-3) [Beil. I_1-(207), I_2-(446)] and of diethylcarbinol (pentanol-3) (1:6175) (reduction products) — $\bar{C}$ with C_6H_5MgBr in ether gives (57% yield (35)) diphenyl-ethyl-carbinol [Beil. VI-687, VI_1-(331)], m.p. 95°, but $\bar{C}$ with C_6H_5MgBr with $CdCl_2$ in ether gives (76% yield (36)) ethyl phenyl ketone (propiophenone) (1:5525).]

[$\bar{C}$ + 2,5-dimethylpyrrole *N*-magnesyl bromide in dry ether gives (by rearr.) (37) 3-propionyl-2,5-dimethylpyrrole, colorless cryst. from AcOH, m.p. 102.5° (37); $\bar{C}$ with benzimidazyl *N*-magnesyl bromide in dry ether yields (38) (39) *N*-(propionyl)benzimidazole, m.p. 125° (38) (39) (corresp. picrate, m.p. 228° (38) (39)).]

[$\bar{C}$ + ethyl acetoacetate + Mg in C_6H_6 refluxed 2 hrs., treated with aq. gives (36% yield (40)) *ethyl α-propionylacetoacetate, b.p. 104–106° at 12 mm. (40) (isolated as Cu enolate,* m.p. 78–79°, blue ndls. from MeOH/aq., violet ndls. from pet. ether (40)).]

[$\bar{C}$ with $FeCl_3$ (1 mole) on warming evolves HCl and gives a prod. which with aq. gives (31% yield (41)) (42) diethyl ketone (1:5420) + CO_2, or with alc. yields (43) ethyl α-propionylpropionate [Beil. III-686, III_1-(436).]

[$\bar{C}$ with equal wt. $ClSO_3H$ stood at room temp. 5–10 days, poured into aq. (44), or $\bar{C}$ with tripropylamine in lgr. (45) gives (cf. (42)) in small yield 3,5-dimethyl-2-ethyl-6-hydroxypyrone-4 [Beil. XVII-453], cryst. from aq. or AcOH, m.p. 151° (45).]

[$\bar{C}$ with olefins or cyclo-olefins (cyclenes) in pres. of cat. adds to unsatn. yielding chloroketones; e.g., $\bar{C}$ with ethylene + $AlCl_3$ at 0° gives (50% yield (46)) (47) β-chloroethyl ketone (1-chloropentanone-3) (3:9268), $\bar{C}$ with trimethylethylene (2-methylbutene-2) (1:8220) + $SnCl_4$ gives (57% yield (48)) 2-chloro-2,3-dimethylhexanone-4, b.p. 74–78° at 17 mm., $D_4^{14} = 0.975$ (48) (note that this prod. on htg. with dimethylaniline loses HCl giving (60% yield (48)) of a mixt. of 2,3-dimethylhexen-2-one-4, b.p. 164–166° at 750 mm., $D_4^{13} = 0.872$, $n_D^{13} = 1.4535$ (semicarbazone, m.p. 200° (48)) and 2,3-dimethylhexen-1-one-4, b.p. 158–162° at 750 mm., $D_4^{13} = 0.862$, $n_D^{13} = 1.4450$ (semicarbazone, m.p. 108–110° (48)); $\bar{C}$ with cyclohexene (1:8070) + $SnCl_4$ gives a prod. which with dimethylaniline loses HCl

to cyclohexen-1-yl ethyl ketone, b.p. 90° at 10 mm., $D_4^{13.5} = 0.981$, $n_D^{13.5} = 1.6005$ (oxime, m.p. 79°, semicarbazone, m.p. 195° (49)). — Note, however, that addn. of C̄ to certain types of olefins is followed by *spontaneous* loss of HCl so that the unsatd. ketone *forms the direct product*; e.g., *C̄ with isobutylene* (2-methylpropene-1) + $SnCl_4$ gives (30% yield (48)) 2-methylhexen-2-one-4, b.p. 147–148° at 760 mm., $D_4^{15} = 0.850$, $n_D^{15} = 1.4496$ (48) (semicarbazone, m.p. 163° (48)).]

[C̄ with aromatic hydrocarbons + cat. evolves HCl yielding *corresp.* ketones: e.g., C̄ with C_6H_6 + $AlCl_3$ in CS_2 gives (84% yield (10)) (50) ethyl phenyl ketone (propiophenone) (1:5525); C̄ with toluene (1:7405) + $AlCl_3$ in CS_2 gives (yields: 60% (51), 50% (52)) (53) ethyl *p*-tolyl ketone [Beil. VII-317, VII_1-(170)], b.p. 238–239°; for analogous reactions of C̄ with *o*-xylene (1:7430) (54), 2-methylnaphthalene (1:7605) (55), anthracene (1:7285) (56), phenanthrene (1:7240) (57), or acenaphthene (1:7225) (58) see indic. refs.; for analogous reactions of C̄ with heterocyclic systems, e.g., C̄ + 2-nitrofuran + $TiCl_4$ (59) or C̄ + *thiophene* + P_2O_5 *at 210° for 10–12 hrs.* (60), see indic. refs.]

[C̄ with alcs. reacts normally yielding *corresp.* esters: e.g., C̄ with MeOH *yields* methyl propionate (1:3020), C̄ with EtOH yields ethyl propionate (1:3070), etc.; for use of Mg in reaction of C̄ with tertiary alcs., e.g., C̄ + *ter*-butyl alc. (1:6140) + Mg giving (68% yield (61)) *ter*-butyl propionate, b.p. 115–116.5° (61), or C̄ + *ter*-amyl alc. (1:6160) + Mg *giving* (75% yield (61)) *ter*-amyl *propionate*, b.p. 153–156° at 710 mm. (61), see indic. refs.]

[C̄ with phenols gives the corresp. phenol esters: e.g., C̄ with phenol gives (62) phenyl propionate (1:3696), etc.; note, however, that these phenol esters on htg. with $AlCl_3$ in appropriate solvents, *especially nitrobenzene, undergo the Fries rearr. yielding o- and p-*propiophenols; this complete sequence is often carried through without *isolation* of the intermediate ester, e.g., for C̄ + phenol + $AlCl_3$ giving directly *o*-hydroxypropiophenone [Beil. VIII-102, $VIII_1$-(547)] (50% yield) and *p*-hydroxypropiophenone [Beil. VIII-102 (25% *yield*) see (63); *for key refs. on direct rearr. of phenyl propionate to these products* see (64) (65); scores of analogous cases with other phenols or their ethers cannot be included here.]

[C̄ with certain hydroxy-azo-compounds in dry ether yields addn. cpds. usually (but *not always*) *of 1:1 type: e.g., C̄ with p-hydroxy-azobenzene* [Beil. XVI-96, XVI_1-(233)], m.p. 152°, in dry ether on stdg. at room temp. ppts. 1:1 cpd., m.p. 162° (66); *for numerous* analogous cases using homologous hydroxy-azo cpds. see (66).]

C̄ hydrolyzes with aq. yielding propionic acid (1:1025); for the amide, anilide, *p*-toluidide, and other derivs. *corresp. to* C̄ *see under propionic acid* (1:1025).

3:7170 (1) Koehl, Wenzke, *J. Am. Chem. Soc.* **59**, 1418 (1937). (2) John, Beetz, *J. prakt. Chem.* (2) **143**, 344 (1935). (3) Sestini, *Bull. soc. chim.* (2) **11**, 470 (1869). (4) Bardan, *Bull. soc. chim.* (4) **49**, 1427 (1931). (5) Martin, Partington, *J. Chem. Soc.* **1936**, 162. (6) Kohlrausch, Pongratz, *Z. physik. Chem.* **B-22**, 381 (1933). (7) Brühl, *Ann.* **203**, 14–15 (1880). (8) Brown, *J. Am. Chem. Soc.* **60**, 1326 (1938). (9) Timmermans, Mataar, *Bull. soc. chim. Belg.* **30**, 216 (1921). (10) Walden, *Z. physik. Chem.* **55**, 222 (1906).

(11) Clark, Bell, *Trans. Roy. Soc. Can.* (3) **27**, III 97–103 (1933). (12) Fourneau, Nicolitch, *Bull. soc. chim.* (4) **43**, 1236–1238 (1928). (13) Fierz-David, Kuster, *Helv. Chim. Acta* **22**, 89 (1939). (14) Linnemann, *Ann.* **148**, 255–257 (1868). (15) Michael, *Ber.* **34**, 4046–4051 (1901). (16) Aschan, *Ber.* **31**, 2346 (1898). (17) Chem. Fabrik vorm. Weiler-ter-Meer, Ger. 350,050, March 11, 1922; *Cent.* **1922**, IV 155. (18) Henle, Schirm (to M. L. B.), Ger. 397,311, July 1, 1924; French 568,331, March 22, 1924; *Cent.* **1924**, II 1401–1402. (19) Read, *J. Am. Chem. Soc.* **44**, 1751 (1922). (20) Montonna, *J. Am. Chem. Soc.* **49**, 2115 (1927).

(21) Colson, *Compt. rend.* **121**, 1155 (1895). (22) Stellmann, French 785,076, Aug. 1, 1935; *Cent.* **1935**, II 3301. (23) Kuster, *Z. physiol. Chem.* **130**, 9–10 (1923). (24) Hertel, Becker, *Z. physik. Chem.* **B-27**, 310–311 (1934). (25) Kharasch, Brown, *J. Am. Chem. Soc.* **62**, 925–929 (1940). (26) Wolffenstein, Rolle, *Ber.* **41**, 735 (1908). (27) Aschan, *Ber.* **45**, 1913–1919 (1912).

(28) Aschan, *Ber.* **46**, 2162 (1913). (29) Kharasch, Hobbs, *J. Org. Chem.* **6**, 709–712 (1941). (30) Anderlini, *Gazz. chim. ital.* **25**, II 132–133 (1895).

(31) Whitby, *J. Chem. Soc.* **1926**, 1462. (32) Mailhe, *Compt. rend.* **180**, 1112 (1925). (33) Anderlini, *Gazz. chim. ital.* **25**, II 48, 129 (1895). (34) Petrov, Roslova, *J. Gen. Chem. (U.S.S.R.)* **10**, 973–976 (1940); *C.A.* **35**, 2467 (1941). (35) Gilman, Fothergill, Parker, *Rec. trav. chim.* **48** 750 (1929). (36) Gilman, Nelson, *Rec. trav. chim.* **55**, 528–530 (1936). (37) Oddo, Acuto, *Gazz. chim. ital.* **65**, 1033 (1935), *Cent.* **1936**, I 3832; *C.A.* **30**, 4857 (1936). (38) Oddo, Raffia, *Gazz. chim. ital.* **67**, 541 (1937), *Cent.* **1938**, I 1581; *C.A.* **32**, 1697 (1938). (39) Oddo, Ingraffia, *Gazz. chim. ital.* **62**, 1096 (1932); *Cent.* **1932**, I 2943. (40) Spassow, *Ber.* **70**, 2383–2384 (1937).

(41) Hamonet, *Bull. soc. chim.* (2) **50**, 356–357 (1888). (42) Wedekind, *Ann.* **323**, 250, 254 (1902). (43) Hamonet, *Bull. soc. chim.* (3) **2**, 335–338 (1889). (44) Krajcinovic, *Ber.* **62**, 579–581 (1929). (45) Wedekind, Haeussermann, *Ber.* **41**, 2299–2302 (1908). (46) Kenner, Statham, *Ber.* **69**, 17 (1936). (47) Schoeller, Züllner (to Schering-Kahlbaum A.G.), U.S. 1,737-203, Nov. 26, 1929, *Cent.* **1930**, II 1133, Brit. 282,412, Feb. 15, 1928, *Cent.* **1929**, I 143. (48) Colonge, Mostafavi, *Bull. soc. chim.* (5) **6**, 335–342; 342–354 (1939). (49) Colonge, Deroux, *Bull. soc. chim.* (5) **7**, 459–468 (1941). (50) Pampel, Schmidt, *Ber.* **19**, 2896 (1886).

(51) Sanchez, *Bull. soc. chim.* (4) **45**, 284 (1929). (52) Willgerodt, Hambrecht, *J. prakt. Chem.* (2) **81**, 76 (1910). (53) Klages, *Ber.* **35**, 2252 (1902). (54) von Auwers, Ziegler, *Ann.* **425**, 260 (1921). (55) Haworth, Bolam, *J. Chem. Soc.* **1932**, 2249. (56) I.G., Brit. 289,585, May 24, 1928; *Cent.* **1928**, II 1036. (57) Bachmann, Struve, *J. Am. Chem. Soc.* **58**, 1659 (1936). (58) Dziewonski, Moszew, *Roczniki Chem.* **11**, 415–425 (1931); *Cent.* **1931**, II 570, *C.A.* **26**, 2975 (1932). (59) Gilman, Burtner, Calloway, Turck, *J. Am. Chem. Soc.* **57**, 908 (1935). (60) Steinkopf, Schubart, *Ann.* **424**, 8–9 (1921).

(61) Spassow, *Ber.* **70**, 1926–1929 (1937). (62) Perkin, *J. Chem. Soc.* **55**, 547–548 (1889). (63) Torres, Amargos, *Anales soc. españ. fís. quím.* **21**, 37–47 (1933), *Cent.* **1933**, II 372; *C.A.* **27**, 1624 (1933). (64) Miller, Hartung, *Org. Syntheses, Coll. Vol. 2* (1st ed.), 543–545 (1943); **13**, 90–92 (1933). (65) von Auwers, Pötz, Noll, *Ann.* **535**, 228–230 (1938). (66) Fischer, Taurinisch, *Ber.* **64**, 236–239 (1931). (67) Schmidt, Schloffer (to I.G.) Ger. 738,398, July 15, 1943; *C.A.* **38**, 3992 (1944).

3:7175 1-CHLOROBUTYNE-2 $CH_3—C{\equiv}C—CH_2Cl$ C_4H_5Cl Beil. S.N. 12

(γ-Methylpropargyl chloride)

B.P. 81–84° (1)

Pale yel. oil.

[For prepn. of C̄ (44% yield) from butyn-2-ol-1 + PCl_5 in ether see (1).]

C̄ in ether/acetone soln. on treatment with K_2CO_3 + phenol gives (57% yield) γ-methylpropargyl phenyl ether, b.p. 123–126° at 25 mm., n_D^{20} = 1.3894 (1).

3:7175 (1) Hurd, Cohen, *J. Am. Chem. Soc.* **53**, 1074–1075 (1931).

3:7195 CHLOROMETHYL ETHYL ETHER C_3H_7OCl Beil. I - 581

$ClCH_2.O.C_2H_5$ I₁-(304) I₂-(645)

B.P. 83° at 763.1 mm.	**(1)**	D_4^{20} = **1.0263** (3)	n_D^{20} = **1.40398** (1)
82°	**(2)**	**1.0127** (1)	
81–82°	**(3)**	D_4^{15} = **1.0188** (1)	n_D^{12} = **1.0282** (3) (7)
80°	**(4)**		
79–80°	**(5) (6)**		

C̄ undergoes some decompn. at b.p.

[For prepn. from ethyl alc. (1:6130) + trioxymethylene (1:0080) + dry HCl see (3) (1); from ethyl alc. + formalin + HCl (42–44% yield (6)) see (6).]

C̄ on shaking with aq. readily hydrolyzes yielding formaldehyde (1:0145), ethyl alc. (1:6130), + HCl.

to cyclohexen-1-yl ethyl ketone, b.p. 90° at 10 mm., $D_4^{13.5} = 0.981$, $n_D^{13.5} = 1.5005$ (oxime, m.p. 79°, semicarbazone, m.p. 195° (49)). — Note, however, that addn. of Č to certain types of olefins is followed by *spontaneous* loss of HCl so that the unsatd. ketone forms the direct product; e.g., Č with isobutylene (2-methylpropene-1) + $SnCl_4$ gives (30% yield (48)) 2-methylhexen-2-one-4, b.p. 147–148° at 760 mm., $D_4^{15} = 0.859$, $n_D^{15} = 1.4496$ (48) (semicarbazone, m.p. 163° (48)).]

[Č with aromatic hydrocarbons + cat. evolves HCl yielding corresp. ketones: e.g., Č with C_6H_6 + $AlCl_3$ in CS_2 gives (84% yield (19)) (50) ethyl phenyl ketone (propiophenone) (1:5525); Č with toluene (1:7405) + $AlCl_3$ in CS_2 gives (yields: 60% (51), 50% (52)) (53) ethyl p-tolyl ketone [Beil. VII-317, VII₁-(170)], b.p. 238–239°; for analogous reactions of Č with o-xylene (1:7430) (54), 2-methylnaphthalene (1:7605) (55), anthracene (1:7285) (56), phenanthrene (1:7240) (57), or acenaphthene (1:7225) (58) see indic. refs.; for analogous reactions of Č with heterocyclic systems, e.g., Č + 2-nitrofuran + $TiCl_4$ (59) or Č + thiophene + P_2O_5 at 210° for 10–12 hrs. (60), see indic. refs.]

[Č with alcs. reacts normally yielding corresp. esters: e.g., Č with MeOH yields methyl propionate (1:3020), Č with EtOH yields ethyl propionate (1:3070), etc.; for use of Mg in reaction of Č with tertiary alcs., e.g., Č + *ter*-butyl alc. (1:6140) + Mg giving (68% yield (61)) *ter*-butyl propionate, b.p. 115–116.5° (61), or Č + *ter*-amyl alc. (1:6160) + Mg giving (75% yield (61)) *ter*-amyl propionate, b.p. 153–156° at 710 mm. (61), see indic. refs.]

[Č with phenols gives the corresp. phenol esters: e.g., Č with phenol gives (62) phenyl propionate (1:3696), etc.; note, however, that these phenol esters on htg. with $AlCl_3$ in appropriate solvents, especially nitrobenzene, undergo the Fries rearr. yielding o- and p-propiophenols; this complete sequence is often carried through without isolation of the intermediate ester, e.g., for Č + phenol + $AlCl_3$ giving directly o-hydroxypropiophenone [Beil. VIII-102, VIII₁-(547)] (50% yield) and p-hydroxypropiophenone (Beil. VIII-102 (25% yield) see (63); for key refs. on direct rearr. of phenyl propionate to these products see (64) (65); scores of analogous cases with other phenols or their ethers cannot be included here.]

[Č with certain hydroxy-azo-compounds in dry ether yields addn. cpds. usually (but not always) of 1:1 type: e.g., Č with p-hydroxy-azobenzene [Beil. XVI-96, XVI₁-(233)], m.p. 152°, in dry ether on stdg. at room temp. ppts. 1:1 cpd., m.p. 162° (66); for numerous analogous cases using homologous hydroxy-azo cpds. see (66).]

Č hydrolyzes with aq. yielding propionic acid (1:1025); for the amide, anilide, p-toluidide, and other derivs. corresp. to Č see under propionic acid (1:1025).

3:7170 (1) Koehl, Wenzke, *J. Am. Chem. Soc.* 59, 1418 (1937). (2) John, Beetz, *J. prakt. Chem.* (2) 143, 344 (1935). (3) Sestini, *Bull. soc. chim.* (2) 11, 470 (1869). (4) Bardan, *Bull. soc. chim.* (4) 49, 1427 (1931). (5) Martin, Partington, *J. Chem. Soc.* 1936, 162. (6) Kohlrausch, Pongratz, *Z. physik. Chem.* B-22, 381 (1933). (7) Brühl, *Ann.* 203, 14–15 (1880). (8) Brown, *J. Am. Chem. Soc.* 60, 1326 (1938). (9) Timmermans, Mataar, *Bull. soc. chim. Belg.* 30, 216 (1921). (10) Walden, *Z. physik. Chem.* 55, 222 (1906).

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3:7175 1-CHLOROBUTYNE-2 $CH_3—C{\equiv}C—CH_2Cl$ C_4H_5Cl Beil. S.N. 12

(γ-Methylpropargyl chloride)

B.P. 81-84° (1)

Pale yel. oil.

[For prepn. of Č (41% yield) from butyn-2-ol-1 + PCl_3 in ether see (1).]

Č in ether/acetone soln. on treatment with K_2CO_3 + phenol gives (57% yield) γ-methylpropargyl phenyl ether, b.p. 123-126° at 25 mm., n_D^{20} = 1.5391 (1).

3:7175 (1) Hurd, Cohen, *J. Am. Chem. Soc.* 53, 1074-1075 (1931).

3:7195 CHLOROMETHYL ETHYL ETHER C_3H_7OCl Beil. I - 581

$ClCH_2.O.C_2H_5$ I_1-(304) I_2-(645)

B.P. 83° at 763.1 mm. (1)		D_4^{20} = 1.0263 (3)	n_D^{17} = 1.40308 (1)
82°	(2)	1.0127 (1)	
81-82°	(3)	D_4^{15} = 1.0188 (1)	n_D^{12} = 1.0282 (3) (7)
80°	(4)		
79-80°	(5) (6)		

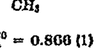
Č undergoes some decompn. at b.p.

[For prepn. from ethyl alc. (1:6130) + trioxymethylene (1:0080) + dry HCl see (3) (1); from ethyl alc. + formalin + HCl (42-44% yield (6)) see (6).]

Č on shaking with aq. readily hydrolyzes yielding formaldehyde (1:0145), ethyl alc. (1:6130), + HCl.

3:7195 (1) Karvonen, *Ann. Acad. Sci. Fennicae*, **3-A**, No. 7, 1–103 (1912): *Cent.* **1912**, II 1269; *C.A.* **14**, 2175 (1920). (2) Litterscheid, *Ann.* **330**, 123 (1904). (3) Farren, Fife, Clark, Garland, *J. Am. Chem. Soc.* **47**, 2421 (1925). (4) Wedekind, *Ber.* **36**, 1385 (1903). (5) de Gaspari, *Gazz. chim. ital.* **27**, II 297 (1897). (6) Foran, *J. Soc. Chem. Ind.* **44**, 173–174T (1925).

3:7200 1-CHLORO-2,2-DIMETHYLPROPANE $C_5H_{11}Cl$ Beil. I - 141
(Neopentyl chloride; I₁-(50)
ter-butylcarbinyl chloride) I₂—



B.P.		F.P.		
84.4°	at 760 mm. (1)	−20° (1) (4)	D_4^{20} = 0.866 (1)	n_D^{20} = 1.4042 (1)
83.9°	at 750 mm. (1)		*0.865* (3)	1.4043 (3)
83.5°	at 740 mm. (1)			
83.3–84.5°	(2)			
82–83.5°	*at 734 mm.* (3)			
24°	at 80 mm. (4)			

[For prepn. of C̄ (30% yield (3)) from neopentane (tetramethylmethane) (1:8499) by chlorination in light at 0° see (4) (3) (1). — C̄ *cannot* (1) (5) (contrary to earlier claims (6)) be prepared from neopentyl alc. (*ter*-butylcarbinol) (1:5812) even with $SOCl_2$ + pyridine (13).]

C̄ is stable for long periods of time even at 200° (1). — C̄ is extraordinarily unreactive giving none of the ordinary alkyl halide reactns. except the formn. of the corresponding Grignard reagent.

C̄ in dil. ether soln. reacts slowly with Mg giving (1) (90% yield (8)) neopentyl MgCl. [For reactn. of R.Mg.Cl with CO_2 see (12).]

[For reactns. of C̄ with C_6H_6 + $AlCl_3$ (2), or with metallic Na (10), or with NaPr (11) see indic. refs.]

C̄ is unchanged after htg. 20 hrs. at 100° with alc. KOH (1) or htg. with CuCN at 90° in a s.t. for 200 hrs. (1) or after treatment with KI in acetone (1) or after 6 hrs. refluxing with 6% Na/Hg (11).

- Ⓓ *ter*-Butylacetanilide (β,β-dimethyl-*n*-butyranilide): m.p. 131° (1), 130–131° (3), 129–130° (3). [From R.MgCl by reactn. with phenyl isocyanate (1).]
- Ⓓ Neopentyl mercuric chloride: m.p. 117–118° (3), 116.5–117° (1). [From RMgCl with $HgCl_2$ (1) (3) in dry ether (90% yield (3)).] [For reactn. of R.MgCl with di-*p*-tolylmercury giving di-neopentylmercury, b.p. 67–69° at 3 mm., m.p. 31–33°, see (9).] [For reactn. of RHgCl with KBr giving 82% yield neopentyl bromide, b.p. 104.8° at 732 mm., or with I_2 giving 92% yield neopentyl iodide, b.p. 70° at 100 mm., see (3).]

3:7200 (1) Whitmore, Fleming, *J. Am. Chem. Soc.* **55**, 4161–4162 (1933). (2) Pines, Schmerling, Ipatieff, *J. Am. Chem. Soc.* **62**, 2901–2902 (1939). (3) Whitmore, Wittle, Popkin, *J. Am. Chem. Soc.* **61**, 1585–1590 (1939). (4) Fleming, Whitmore, *J. Am. Chem. Soc.* **54**, 3460–3461 (1932). (5) Whitmore, Rothrock, *J. Am. Chem. Soc.* **54**, 3431–3435 (1932). (6) Tissier, *Ann. chim.* (6) **29**, 344 (1893). (7) Richard, *Ann. chim.* (8) **21**, 341–342 (1910). (8) Whitmore, Wittle, Harriman, *J. Am. Chem. Soc.* **61**, 1585–1586 (1939). (9) Whitmore, Rohrmann, *J. Am. Chem. Soc.* **61**, 1591–1592 (1939). (10) Whitmore, Popkin, Bernstein, Wilkins, *J. Am. Chem. Soc.* **63**, 124–127 (1941).

(11) Whitmore, Zook, *J. Am. Chem. Soc.* **64**, 1783–1785 (1942). (12) Bush, *J. Am. Chem. Soc.* **61**, 965 (1939). (13) Whitmore, Karnatz, *J. Am. Chem. Soc.* **60**, 2534 (1938).

3:7205 1-CHLOROBUTENE-2 $CH_3CH{=}CH.CH_2Cl$ C_4H_7Cl Beil. I - 205
(Crotonyl chloride, I_1—
α-chloro-β-butylene, γ-methylallyl chloride) I_2-(176)

B.P. 84° at 750 mm. (1)	D_4^{20} = 0.9340 (3)	n_D^{20} = 1.4350 (1) (2) (17)
84–85° (2)	0.9316 (7)	1.4351 (5)
83.8° (3)		1.4352 (7)
83° (7)		1.4356 (3)
80° (4)		1.4359 (6)
45.6–45.7° at 191 mm. (5)		
43.7–44.0° at 177 mm. (5)		
−2° at 18 mm. (6)		

Because of the close interrelationship of C̄ with the isomeric 3-chlorobutene-1 (3:7090) some confusion exists regarding the nomenclature. The compound here described (1-chlorobutene-2) is by some authors designated as crotyl chloride; this name, however, is better reserved for the equilibrium mixture of 1-chlorobutene-2 and 3-chlorobutene-1 as indicated by (7).

Pure C̄ (in the absence of catalysts) is quite stable (1) and may be kept at room temperature as long as a year (5) without significant increase in n_D^{20}. However, in the presence of $FeCl_3$, HCl, or $CuCl_2$ + HCl, C̄ is in part isomerized to 3-chlorobutene-1 and an equilibrium mixt. is formed. The composition of this equilibrium mixt. depends upon the temperature, catalyst, and other factors. E g., with $FeCl_3$ the equilibrium mixt. conts. 50% C̄; with 1 mole HCl it conts. 75% C̄. Although the two compounds can easily be separated by careful fractional distillation (5) yet consideration must always be given to the possible formation during chem. reaction of the derivatives of the other isomer. The refractive index of mixts. of 1-chlorobutene-2 and 3-chlorobutene-1 is a linear function of the composition (1). Although *cis* and *trans* stereoisomers of C̄ are possible, no record of their isolation has been published.

[For the prepn. of a mixt. of C̄ + 3-chlorobutene-1 from butadiene-1,3 + HCl see (1) (7) (8) (9); for prepn. of C̄ from crotonyl alcohol with PCl_3 + pyridine see (3) (6), with HCl + Cu_2Cl_2 see (1), with conc. HCl see (5).]

C̄ passed over soda-lime in an iron furnace at 530–550° yields (11) butadiene-1,3. [Use in prepn. of 1,2,3,4-tetrabromobutane (11).]

[For study of reactivity of C̄ with KI soln. at 20° or NaOEt soln. at 20° and 50° see (3); for reaction with Mg, Zn, etc., see (12); for use in formn. of cellulose ethers see (13); for study of hydrolysis of C̄ under various conditions see (16); for behavior of C̄ with cuprous cyanide see (17).]

—— **Crotonyl 3,5-dinitrobenzoate:** cryst. from alc., m.p. 54° (9). [This cpd. has never been reported from C̄ but only (cf., however (15)) from the corresp. bromide via reaction with silver 3,5-dinitrobenzoate in ether (9); it is possible that the material of m.p. 54° represents a mixt. of the two esters corresponding to crotonyl bromide and the isomeric 3-bromobutene-1 since from the former a 3,5-dinitrobenzoate, m.p. 51°, 50–51° (15), and from the latter a 3,5-dinitrobenzoate, m.p. 59°, have been reported (14).

3:7205 (1) Kharasch, Kritchevsky, Mayo, *J. Org. Chem.* **2**, 494–496 (1938). (2) Baudrenghien, *Bull. soc. chim. Belg.* **31**, 168 (1922). (3) Tamele, Ott, Marple, Hearne, *Ind. Eng. Chem.* **33**, 118–119 (1941). (4) Ganguly, *J. Indian Chem. Soc.* **13**, 584 (1936). (5) Roberts, Young, Winstein, *J. Am. Chem. Soc.* **64**, 2163 (1942). (6) Böhme, *Ber.* **71**, 2378–2379 (1938). (7) Henne, Chanan, Turk, *J. Am. Chem. Soc.* **63**, 3474–3476 (1941). (8) Dykstra (to du Pont), U.S. 2,123,504, July 12, 1938; *Cent.* **1939**, II 2840, *C. A.* **32**, 6666 (1938). (9) Voigt, *J. prakt. Chem.* (2) **151**, 310 (1938). (10) Charon, *Ann. chim.* (7) **17**, 228–230 (1899).

(11) Jacobson, *J. Am. Chem. Soc.* **54**, 1546 (1932). (12) Young, Eisner, *J. Am. Chem. Soc.* **63**, 2113–2115 (1941). (13) Hahn (to du Pont), U.S. 2,082,797, June 8, 1937; *Cent.* **1937**, II 3838; *C.A.* **31**, 5577 (1937).
Kenner, *J. Chem. Soc.* **1935**,
(17) Lane, Fentress, Sherwoc

3:7210 1-CHLOROBUTADIENE-1,3 C_4H_5Cl Beil. S.N. 12

$H_2C{=}CH{-}CH{=}CH{-}Cl$

B.P. 85° (1) $D_{23}^{23} = 0.9601$ (2) $n_D^{20} = 1.470$ (3)
68° (2) $n_D^{23} = 1.4733$ (2)

[For prepn. of $\bar{C}$ from either 1,2-dichlorobutene-3 (3:5350) or 1,4-dichlorobutene-2 (3:5725) by htg. with 2 pts. powdered KOH to about 90° see (1) (3); from solid 1,1,2,3,4-pentachlorobutane (3:0750) in 80% yield (2) or from liq. diastereoisomer (3:9068) in 60% yield (2) with Zn dust in alc. see (2).]

$\bar{C}$ on stdg. (1) (2) polymerizes to a dark resinous mass (4).

3:7210 (1) Muskat, Northrup, *J. Am. Chem. Soc.* **52**, 4054–4055 (1930). (2) Prins, *Rec. trav. chim.* **56**, 119–125 (1937). (3) Muskat (to du Pont), U.S. 2,038,593, Apr. 28, 1936; *Cent.* **1936**, II 3359; *C.A.* **30**, 3912 (1936). (4) I. G. Farbenindustrie, French 769,472, Aug. 27, 1934; *Cent.* **1935**, I 1946.

3:7212 CHLOROACETALDEHYDE $Cl{-}CH_2{-}CHO$ C_2H_3OCl Beil. I - 610
I_1-(327)
I_2-(675)

B.P. 85–86° (1)
85.0–85.5° cor. at 748 mm. (2)
84.5–85° at 759 mm. (3)

Colorless liq. with sharp and penetrating odor; vigorously attacks mucous membrane. — $\bar{C}$ with aq. forms (2) a crystn. hemihydrate, $\bar{C}.\frac{1}{2}H_2O$; this does not have a sharp m.p. but about 43–50° begins to liquefy and on further htg. yields $\bar{C}$, whose vapor may be dried by passing over anhydr. $CuSO_4$ (2) (3); this hemihydrate is sol. in aq. from which it may be recovered by evaporation in a stream of dry CO_2; it is also sol. in alc. or ether, sepg. unchanged on evapn. of solvent (2) (for prepn. (60% yield) from glycerol α-monochlorohydrin (3:9038) by oxidn. with HIO_4 see (40)). — $\bar{C}$ also forms (4) with EtOH a liq. chloroacetaldehyde ethylalcoholate (chloroacetaldehyde ethyl-hemi-acetal), but in excess alc. on protracted stdg. at room temp. (4) this is converted to chloroacetaldehyde diethylacetal (3:8228), or on treatment with dry HCl yields (4) α,β-dichloroethyl ethyl ether (3:5640).

[For prepn. of $\bar{C}$ from its crystn. trimer (3:2300) by distn. at ord. press. see (2) (5) (6); from chloroacetaldehyde diethylacetal (3:8228) by htg. at 150° in CO_2 with anhydr. oxalic acid (2), AcOH (2), or dil. H_2SO_4 (2) (7) see indic. refs.; from chloroacetaldehyde ethylalcoholate (see above) by htg. with anhydr. oxalic acid at 150° (90% yield) see (8) (note that the actn. of Cl_2 on paraldehyde (1:0170) gives acc. to conditions either $\bar{C}$ (9) or α,α,β-trichloro-*n*-butyraldehyde (butylchloral) (3:5910) (10) (11)).]

[For prepn. of $\bar{C}$ from vinyl chloride (3:7010) with Cl_2 + aq. in the dark at 35° see (12) (13) (14) (15); from methylene dichloride (3:5020) with formaldehyde + SO_2Cl_2 at 300° with cat. see (16); from α,β-dichloroethyl ethyl ether (3:5640) with conc. H_2SO_4 see (17); from α,β-dichloroethyl acetate on distn. with a little $ZnCl_2$ (acetyl chloride also formed) (18) or from α,β-dichloroethyl benzoate similarly (benzoyl chloride also being formed) (19) or from α,β-dichloroethyl laurate (lauroyl chloride also being formed) (19) see indic. refs.]

[For formn. of C̄ from sodium β,β-dichloro-α-hydroxypropionate on boilg. with aq. see (20); from β-chloroethylidene-diurethane on warming with dil. HCl see (21); from acetaldehyde (1:0100) with ethyl hypochlorite followed by distn. with anhydr. oxalic acid see (22); from chloroacetaldehyde-sulfonic acid [Beil. I_2-(818)] by treatment with steam in 60% H_2SO_4 (23) or by htg. with 80% H_2SO_4 (24) see indic. refs.]

C̄ gives positive fuchsin-aldehyde test (1). — C̄ reduces $NH_4OH/AgNO_3$ on warming (2).

C̄ does not oxidize in the air (2) but is oxidized by conc. HNO_3 (2) (20) or by AgOH (20) or by dil. H_2O_2 (25) to chloroacetic acid (3:1370). — C̄ on treatment as directed (26) with halogen magnesium alcoholate (e.g., EtOMgCl) is reduced to β-chloroethanol (3:5552).

C̄ on stdg. in s.t. is rapidly converted to an amorphous polymer (2); C̄ (or its hemihydrate) on shaking with ½ vol. cold conc. H_2SO_4 yields (1) a cryst. trimer, 2,4,6-tris-(chloromethyl)-trioxane-1,3,5 (3:2300), m.p. 87–87.5°, which on distn. at ord. press. depolymerizes to C̄.

The hemihydrate of C̄ htd. *alone or in pres. of a few drops of conc. H_2SO_4 condenses* with itself yielding (27) (28) *α,γ-dichlorocrotonaldehyde* [Beil. I-731, I_2-(789)].

[C̄ warmed with EtOH (4) or the ethylalcoholate of C̄ in EtOH treated with dry HCl gas (8) yields chloroacetaldehyde diethylacetal (3:8228), b.p. 157°, and in the latter case also (4) α,β-dichloroethyl ethyl ether (3:5640).]

[C̄ with KCN yields (29) (7) an oily prod. (cyanohydrin?) which by hydrolysis with HCl gives β-chlorolactic acid [Beil. III-286, III_1-(110), III_2-(209)] + AcOH, C̄ + NaCN+ BzCl yields (30) α-benzoxy-β-chlorolactonitrile; note, however, that C̄ boiled with alc. KCN yields (31) EtOAc, or with aq. KCN yields (31) AcOH.]

[For behavior of C̄ with AcCl (2), Ac_2O (32), see indic. refs.; C̄ with ethyl diazoacetate yields (3) ethyl γ-chloroacetoacetate (3:6375); C̄ with EtMgBr in ether yields (6) 1-chlorobutanol-2 (3:8025); C̄ with nitromethane as directed (33) yields 1-chloro-3-nitropropanol-2, with nitroethane, 1-chloro-3-nitrobutanol-2; C̄ with thioformamide (35) or C̄ + formamide + P_2S_5 (34) yields thiazole [Beil. XXVII-15, $XXVII_1$-(207)], m.p. 116°.]

—— **Chloroacetaldoxime:** lachrymatory oil dec. on distn. at 10 mm. (36). [From C̄ with 4 moles $NH_2OH.HCl$ (36).]

Ⓓ **Chloroacetaldehyde semicarbazone:** ndls. from alc., m.p. 148° (37), 134–135° dec. (38), 134° (40). [From C̄ + semicarbazide hydrochloride + NaOAc (37).]

—— **Chloroacetaldehyde dimethone:** unreported. [Note that C̄ with warm alc. soln. of "dimethone" ("dimedone") (dimethyldihydroresorcinol) not only condenses normally but also loses HCl yielding (39) same prod., m.p. 227° u.c., 237.5° cor. (39), *as obtd. from hydroxyacetaldehyde.*]

3:7212 (1) Jones, Williams, *J. Chem. Soc.* **1934**, 834. (2) Natterer, *Monatsh.* **3**, 442–464 (1882). (3) Schlotterbeck, *Ber.* **42**, 2570–2571 (1909). (4) Natterer, *Monatsh* **5**, 494–499 (1884). (5) Späth, *Monatsh.* **36**, 6–7 (1915). (6) Helferich, Speidel, *Ber.* **54**, 2634–2635 (1921). (7) Frank, *Ann.* **206**, 339–344 (1880). (8) Fritsch, Schumacher, *Ann.* **279**, 307–308 (1894). (9) Freundler, *Bull soc. chim* (4) **1**, 70 (1907). (10) Krämer, Pinner, *Ber.* **3**, 385 (1870); *Ann.* **158**, 41–42 (1871).

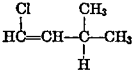
(11) Pinner, *Ann.* **179**, 26 (1875). (12) Ernst, Lange (to I.G.), U S. 1,806,285, May 19, 1931; *Cent.* **1931**, II 1632; *C A.* **25**, 3671 (1931); Brit. 299,319, Oct. 22, 1937; *Cent.* **1930**, I 129; *C.A.* **23**, 3235 (1929), Ger. 496,062, Oct. 23, 1927; *Cent.* **1930**, I 3722; *C.A.* **24**, 3251 (1930); French 662,361, Aug. 6, 1929; *Cent* **1930**, I 129. (13) Brit. 299,722, Oct. 28, 1927; *C.A.* **23**, 3479 (1929). (14) N. V. de Bataafsche Petroleum Maatschappij, French 787,529, Sept. 24, 1935; *Cent.* **1936**, II 2227; *C.A* **30**, 1067 (1936). (15) Groll, Hearne (to Shell Development Co.), U.S. 2,060,303, Nov. 10, 1936; *Cent.* **1937**, I 4155; *C.A.* **31**, 419 (1937). (16) Frohlich, Wiezevich (to Standard Oil Development Co), U.S. 2,042,303, May 26, 1936; *Cent.* **1936**, II 3193; *C.A.* **30**, 4871 (1936); Ger. 629,897; May 26, 1936; *Cent.* **1936**, II 2448; *C.A.* **30**, 6006 (1936). (17) Jacobsen, *Ber.* **4**, 216 (1871). (18) Soc. des Usines Chimiques Rhone-Poulenc, Brit. 329,721, June 19, 1930; *Cent.* **1930**, II 1611; *C.A.* **24**, 5767 (1930). (19) Soc. des Usines Chimiques Rhone-Poulenc, Ger. 527,874, June 22, 1931; *Cent.* **1931**, II 1350. (20) Reisse, *Ann.* **257**, 334–336 (1890).

(21) Houben, *J. prakt. Chem.* (2) **105**, 15 (1923). (22) Goldschmidt, Endres, Dirsch, *Ber.* **58**,

576–577 (1925). (23) Lepouse, *Bull. soc. chim. Belg.* **34**, 141–142 (1925). (24) Chem. Fabrik Weiler-ter-Meer, Ger. 362,744, Oct. 31, 1922; *Cent.* **1923**, II 1246. (25) Filachione, *J. Am. Chem. Soc.* **61**, 1706 (1939). (26) I.G., Brit. 384,156, Dec. 22, 1932; *Cent.* **1933**, I 1351. (27) Natterer, *Monatsh.* **4**, 539–543 (1883). (28) Lespieau, *Bull. soc. chim.* (4) **43**, 200–201 (1928). (29) Glinsky, *Ber.* **6**, 1256–1257 (1873). (30) MacCorquodale, Johnson, *Rec. trav. chim.* **51**, 486 (1932).

(31) Chattaway, Irving, *J. Chem. Soc.* **1929**, 1043. (32) Späth, *Monatsh.* **36**, 36 (1915). (33) I. G. French 804,589, Oct. 27, 1936; *Cent.* **1937**, I 1791; *C.A.* **31**, 3505 (1937). (34) Hromatka (to E. Merck), Ger. 670,131, Jan. 12, 1939; *Cent.* **1939**, I 2296; *C.A.* **33**, 2909 (1939). (35) Willstätter, Wirth, *Ber.* **42**, 1918 (1909). (36) Meister, *Ber.* **40**, 3442 (1907). (37) Blaise, *Bull. soc. chim.* (4) **15**, 671–672 (1914). (38) Kling, *Bull. soc. chim.* (4) **5**, 415 (1909). (39) Vorlander, *Z. anal. Chem.* **77**, 254–255 (1929). (40) Hatch, Alexander, *J. Am. Chem. Soc.* **67**, 688 (1945).

3:7215 *d,l*-1-CHLORO-3-METHYLBUTENE-1 C_5H_9Cl **Beil. I - 214**
(*d,l*-4-Chloro-2-methylbutene-3) I_1— I_2—

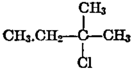


B.P. 85–87° (1)
91–96° (2)

[For prepn. of C̄ from 4,4-dichloro-2-methylbutane (3:7885) with alc. KOH see (1); from 3,4-dichloro-2-methylbutane (3:8075) with alc. NaOH see (2) (note, however, that the latter process very probably leads to a mixt. of C̄ with other prods.).]

3:7215 (1) Bruylants, *Ber.* **8**, 413–414 (1875). (2) Kondakow, *Ber.* **21** *Referate*, 439 (1888).

3:7220 2-CHLORO-2-METHYLBUTANE $C_5H_{11}Cl$ **Beil. I - 134**
(*ter*-Amyl chloride; I_1-(46)
dimethyl-ethyl-carbinyl chloride) I_2-(100)



B.P.			F.P.				
86°		(1) (2) (11)	**−73.7°**	(9)	D_4^{20} = **0.8658**	(5)	
86.0–86.1°		(3)	**−72.7°**	(4)	**0.8650**	(28)	
85.65°	at 760 mm.	(4)	**M.P.**				
85.4–85.6°	at 762 mm.	(5)	**−73.3°**	(9)	$D_4^{13.5}$ = **0.86989**	(10)	
84.5°	at 759 mm.	(28)				n_D^{20} = **1.4058**	(5)
83.0–84.5°	at 744 mm.	(6)				**1.40520**	(28)
51°	at 238 mm.	(7)				**1.4055**	(7)
37–38°	at 150 mm.	(8)					
						$n_D^{13.5}$ = **1.4082**	(10)

C̄ with aq. forms binary const.-boilg. mixt., b.p. 76° (2); C̄ with aq. + *ter*-amyl alc. (1:6160) forms a ternary const.-boilg. mixt. (2).

[For prepn. of C̄ from *ter*-amyl alc. (1:6160) with HCl gas see (11); with conc. HCl (yield: 93–98% (12), 65% (13)) see (12) (13); with PCl_3 (41% yield (6)) or PCl_3 + $ZnCl_2$ (98% yield (14)) see (6) (14); with PCl_5 (80% yield (14)) see (1) (14); with $SOCl_2$ (yield: 99% (14), 41% (6)) see (14) (6); with acetyl chloride see (6); with oxalyl chloride (3:5060) (yield 18% (6)) see (15) (6); with diphosgene (3:5515) see (16); with *p*-nitrobenzoyl chloride see (17).]

[For prepn. of C̄ from isopropyl-methyl-carbinol (2-methylbutanol-3) (1:6170) by

rearr. with conc. HCl + $ZnCl_2$ (80% yield (7)), or with HCl on long stdg. (97% yield (7)), or with PCl_5 (76% yield (7)), or with $SOCl_2$ + pyridine (73% yield (7)) see (7).]

[For prepn. of Č from *trimethylethylene (2-methylbutene-2) (1:8220) by addn. of* HCl see (18) (19) (20); from isopropylethylene (3-methylbutene-1) (1:8200) see (5).]

[For formn. of Č from 2-methylbutane (isopentane) (1:8500) by shaking 2 min. with diisobutylene hydrochloride (3:8113) + $AlCl_3$ see (29).]

Č very rapidly loses HCl by boilg. aq., e.g., 88.6% in 15 min., 94.9% in 30 min., 95.4% in 60 min. (7). Note that hydrolysis with *hot* aq. or aq. Na_2CO_3 gives exclusively olefins (20) (6) but that with *cold* aq. or *cold* aq. NaOH some *ter*-amyl alc. *(1:6160) is also formed* (20), although the latter may result from hydration of the olefin. [For further studies of hydrolysis of Č see (2) (6) (20) (21) (22).]

Č on passing over $BaCl_2$ + soda-lime at 350–400°C *gives* (85% *yield* (5)) a mixture of trimethylethylene (2-methylbutene-2) (1:8220) + *unsym.*-ethyl-methyl-ethylene (2-methylbutene-1) *(1:8210).*

Č with Mg in dry ether gives (yield: 73.6% (23), 38% (26)) RMgCl; this with CO_2 gives (60% yield (13)) dimethyl-ethyl-acetic acid (1:1113) q.v. (see also derivatives below).

Č with Ag 3,5-dinitrobenzoate does *not* (24) yield expected *ter*-amyl 3,5-dinitrobenzoate.

Ⓓ **Dimethyl-ethyl-acetanilide:** m.p. 90–91° u.c. (25), 92° cor. (26), 91.4° (27). [From RMgCl + phenyl isocyanate (25) (26).] [Note that this same product results by rearr., however, from similar treatment of the RMgCl cpds. from 3-chlor-2-methylbutane (3:7275) *q.v.*]

Ⓓ **Dimethyl-ethyl-acet-*p*-toluidide:** m.p. 83.0–83.5° u.c. (25), 83.3° (27). [From RMgCl + *p-tolyl isocyanate (25).*]

Ⓓ **Dimethyl-ethyl-acet-α-naphthalide:** m.p. 137–138° u.c. (25). [From RMgCl + α-naphthyl isocyanate (25).]

3:7220 (1) Wyschnegradsky, *Ann.* **190**, 336 (1877). (2) Ayres, *Ind. Eng. Chem.* **21**, 899–904 (1929). (3) Brearley, Kistiakowsky, Stauffer, *J. Am. Chem. Soc.* **58**, 44–46 (1936). (4) Timmermans, *Bull. soc. chim. Belg.* **30**, 66 (1921). (5) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* **52**, 521–524 (1933). (6) French, Schaefer, *J. Am. Chem. Soc.* **57**, 1576–1578 (1935). (7) Whitmore, Johnston, *J. Am. Chem. Soc.* **60**, 2265–2266 (1938). (8) Simons, Fleming, Whitmore, Bissinger, *J. Am. Chem. Soc.* **60**, 2267–2269 (1938). (9) Turkevich, Smyth, *J. Am. Chem. Soc.* **64**, 737 (1942). (10) Jahn, Möller, *Z. physik. Chem.* **13**, 389 (1894).

(11) Bruchet, *Ann. chim.* (7) **10**, 354 (1897). (12) Norris, Watt, Thomas, *J. Am. Chem. Soc.* **38**, 1076 (1916). (13) Corson, Thomas, Waugh, *J. Am. Chem. Soc.* **51**, 1950 (1929). (14) Clark, Streight, *Trans. Roy. Soc. Can.* (3) **23**, III 77–89 (1929). (15) Adams, Weeks, *J. Am. Chem. Soc.* **38**, 2518–2519 (1916). (16) Nekrassow, Melnikow, *J. prakt. Chem.* (2) **127**, 216–217 (1930). (17) Meisenheimer, *Ann.* **442**, 202 (1925). (18) Michael, Zeidler, *Ann.* **385**, 269–270 (1911). (19) Aschan, *Ber.* **51**, 1304–1306 (1918). (20) Woodburn, Whitmore, *J. Am. Chem. Soc.* **56**, 1394–1395 (1934).

(21) Hughes, *J. Am. Chem. Soc.* **57**, 708–709 (1935). (22) Hughes, McNulty, *J. Chem. Soc.* **1937**, 1283–1291. (23) Whitmore, Badertscher, *J. Am. Chem. Soc.* **55**, 1562 (1933). (24) Tseng, Chu, *Natl. Central Univ. (Nanking), Sci. Rept., Ser. A-1*, No. 2, 5–7 (1931); *C.A.* **26**, 2116 (1932); *Cent.* **1933**, I 669. (25) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2119 (1934). (26) Schwartz, Johnson, *J. Am. Chem. Soc.* **53**, 1065 (1931). (27) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933). (28) Vogel, *J. Chem. Soc.* **1943**, 638, 640. (29) Bartlett, Condon, Schneider, *J. Am. Chem. Soc.* **66**, 1537 (1944).

3:7225 4-CHLOROBUTADIENE-1,2 C_4H_5Cl Beil. S.N. 12

$$\begin{array}{l}\mathrm{Cl}\\ |\\ \mathrm{H_2C{-}CH{=}C{=}CH_2}\end{array}$$

B.P. 88° (1)

Č represents the initial step in the formn. of 3-chlorobutadiene-1,3 ("Chloroprene") (3:7080) by addn. of aq. HCl (1) (2) to vinylacetylene; under certain conditions Č can

be isolated as the major reactn. product, but it readily undergoes isomerization to "Chloroprene" especially in the presence of certain salts, e.g., CuCl (3). When sufficient HCl is present the reactn. proceeds further (1) with formn. of 2,4-dichlorobutene-2 (3:5550).

$\bar{C}$ shaken with 3 pts. 18% HCl contg. CuCl for 16 hrs. at 20° gives (4) (3) (2) butadiene-1,3 ("Chloroprene") (3:7080), the rest being chloroprene polymer. — $\bar{C}$ with 3% dry $FeCl_3$ spontaneously evolves heat and yields (4) chloroprene (3:7080).

$\bar{C}$ stirred with aq. Na_2CO_3 at 60–90° for 15 hrs. gives (10) (50% yield (4)) 4-hydroxybutadiene-1,2, colorless lachrymatory, strongly vesicant liq. with sharp pungent odor, misc. aq. and org. solvents, b.p. 126–128° at 756 mm., 68–70° at 53 mm., $D_4^{20} = 0.9164$, $n_D^{20} = 1.4759$. [This prod. on cat. hydrogenation gives (4) butanol-1 (1:6180) but is unaffected by refluxing with alc. NaOEt, 25% aq. H_2SO_4, or 2% aq. HCl; for many other reactns. and derivatives see (4) (10).]

$\bar{C}$ in 80% alc. or in acetone with NaI, stood for 3 hrs. then diluted with aq., gives (46% yield (4)) 4-iodobutadiene-1,2, b.p. 43–45° at 38 mm., $D_D^{20} = 1.7129$, $n_D^{20} = 1.5709$ (4), which on htg. at 125–130° polymerizes vigorously to iodoprene. — $\bar{C}$ with alc. NaCN yields (5) 4-cyanobutadiene-1,3 (β-vinylacrylonitrile), b.p. 135–138° at 760 mm., 65–68° at 58 mm., 48–50° at 28 mm., $D_4^{20} = 0.8644$, $n_D^{20} = 1.4880$ (5). — $\bar{C}$ with liq. NH_3 at −40 to −50° yields (6) (7) *tris*-(butadien-1,2-yl-4)amine (for extension to many other amines see (7)).

$\bar{C}$ added dropwise to 3 vols. conc. H_2SO_4 at −5° to +3°, then poured onto ice, yields (1) 4-chlorobutanone-2 (3:7640), b.p. 120–122° at 760 mm. (1).

$\bar{C}$ with Cl_2 yields (8) (9) mixt. of 2,3,4-trichlorobutene-1 (3:9064) and 1,2,4-trichlorobutene-2 (3:9062) which reacts further to produce 1,2,2,3,4-pentachlorobutane (3:9070).

$\bar{C}$ in aq. Na_2CO_3 suspension, oxidized with $KMnO_4$, yields (1) chloroacetic acid (3:1370), but neither acetic acid nor oxalic acid. — $\bar{C}$ in $CHCl_3$ treated with O_3 for 12 hrs. at 0°, then with aq., yields (1) formaldehyde (1:0145) and chloroacetaldehyde (3:7212) (the latter not detected directly but only after $KMnO_4$ oxidn. (1) to chloroacetic acid (3:1370)).

3:7225 (1) Carothers, Berchet, Collins, *J. Am. Chem. Soc.* **54**, 4066–4070 (1932). (2) Klebanskii, Tzyurikh, Dolgopol'skii, *Bull. acad. sci. (U.R.S.S.)* **1935**, No. 2, 189–226; *Cent.* **1935**, II 3843 *C.A.* **30**, 1259 (1936) (full English translation in *Rubber Chem. Tech.* **9**, 383–408 (1936). (3) Carothers (to du Pont), U.S. 2,104,789, Jan. 11, 1938; *Cent.* **1939**, I 4108; *C.A.* **32**, 1718 (1938). (4) Carothers, Berchet, *J. Am. Chem. Soc.* **55**, 2811–2813 (1933). (5) Coffman, *J. Am. Chem. Soc.* **57**, 1981–1984 (1935). (6) I. G. Farbenindustrie, French 815,312, July 9, 1937; *Cent.* **1937**, II 2750; *C.A.* **32**, 958 (1938). (7) Carothers, Berchet (to du Pont), U.S. 2,136,177, Nov. 8, 1938; *Cent.* **1939**, I 2497; *C.A.* **33**, 1344 (1939). (8) Carothers, Berchet, *J. Am. Chem. Soc.* **55**, 1628–1631 (1933). (9) Carothers, Berchet (to du Pont), U.S. 1,965,369, July 3, 1934; *Cent.* **1935**, I 3724; *C.A.* **28**, 5716 (1934). (10) Carothers, Berchet (to du Pont), U.S. 2,073,363, March 9, 1937; *Cent.* **1938**, I 1236; *C.A.* **31**, 3503 (1937).

3:7230 1,1-DICHLOROPROPANE $CH_3.CH_2.CHCl_2$ $C_3H_6Cl_2$ Beil. I - 105
(Propylidene (di)chloride) I_1—
I_2—

B.P. 88.3°	(1)	$D_4^{20} = 1.1321$ (1)	$n_D^{20} = 1.4288$ (1)
87–88° at 750 mm.	(2)		1.4295 (2)
86.8–87.6°	(3)		
86°	(4)		

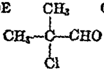
[For prepn. from propionaldehyde (1:0110) with PCl_5 (36–37% yield (1)) together with other products see (1) (3) (5); for formn. (19.6%) (together with other products) from propane by vapor-phase chlorination at 400° see (6) (7) (8); for formn. from 1-chloropropene-1 (3:7030) by addn. of HCl at 0° in presence of $FeCl_3$ see (2).]

$\bar{C}$ on hydrolysis yields propionaldehyde (1:0110); for study of behavior of $\bar{C}$ with boilg. aq. + trace of $NaHCO_3$ or with boilg. aq. + Fe see (6).

$\bar{C}$ with alc. KOH yields (5) 1-chloropropene-1 (3:7030) q.v.

3:7230 [illegible] *J. Am. Chem. Soc.* 63, 2477 (1941). (2) Kharasch, Engel- [illegible] 65, 106 (1935). [illegible] II 458- [illegible] 1941). [illegible] Hass, [illegible] June 4, 1935; *Cent.* 1936, I 1500.

3:7235 α-CHLORO-ISOBUTYRALDEHYDE (2-Chloro-2-methylpropanal-1)



C_4H_7OCl Beil. I - 675; I_1—; I_2—

B.P. 90° (1) (2) $D_4^{15} = 1.053$ (1) (2)

Colorless liq with piquant odor suggestive of chloral.

[For prepn. of $\bar{C}$ from 2-methylpropanol-1 (isobutyl alc.) (1:6165) with Cl_2 see (1) (2); from α,β-dichloroisobutyl isobutyl ether (see below) by htg. with aq. at 100° see (1) (2); from α-chloroisobutyraldehyde diisobutylacetal (see below) with anhydrous oxalic acid (1:0535) or with Ac_2O (1:1015) on htg. see (2); $\bar{C}$ is *not* (2) formed by chlorination of isobutyraldehyde (1:0120).]

$\bar{C}$ reduces Tollens' reagt., Fehling's soln., or $KMnO_4$ (1) (2); $\bar{C}$ on oxidn. with alk. $KMnO_4$ yields (2) α-hydroxyisobutyric acid (1:0431), m.p. 79°.

$\bar{C}$ adds $NaHSO_3$ yielding a compd. from which $\bar{C}$ is regenerated with difficulty (1) (2).

$\bar{C}$ on shaking with conc. H_2SO_4 (½ vol.) yields (1) (2) the corresp. trimer, viz., para-α chloro-isobutyraldehyde (2,4,6-*tris*-(α-chloroisopropyl)trioxane-1,3,5) (3:3220), m.p. 107° (1) (2).

[$\bar{C}$ with isobutyl alc. (1:6165) treated with HCl gas gives (2) α,β-dichloroisobutyl isobutyl ether, b.p. 192.5° at 760 mm., 83° at 15 mm., $D_4^{15} = 1.031$, $n_D^{19} = 1.437$ (2), also obtd. from isobutyl alc. directly with Cl_2 in the cold (2); note that this prod. with aq. on htg. gives $\bar{C}$ + α-chloroisobutyraldehyde di-isobutylacetal, b.p. 218° at 760 mm., 102° at 15 mm., $D_4^{15} = 0.9355$, $n_D^{17} = 1.428$ (2).]

[$\bar{C}$ (or the above α-chloroisobutyraldehyde di-isobutylacetal) with ethyl carbamate satd. with HCl gas gives (2) α-chloroisobutylidene *bis*-urethane $(CH_3)_2C(Cl).CH(NH.COOC_2H_5)_2$, m.p. 122° (2).]

[For complex behavior of $\bar{C}$ with MeMgBr see (3).]

—— α-Chloro-isobutyraldoxime: m.p. 96–97° (4). [Prepd. indirectly from isobutylene with amyl nitrite + HCl (4).]

3:7235 (1) Brochet, *Bull. soc. chim.* (3) 7, 641–644 (1892). (2) Brochet, *Ann. chim.* (7) 10, 352–382 (1897). (3) Henry, *Bull acad. roy. Belg.* 1907, 162–189; *Cent.* 1907, II 445; *Rec. trav. chim.* 26, 410, 425–429 (1907); *Compt. rend.* 144, 308 (1907). (4) Ipatiev, Ssolonina, *J. Russ. Phys.-Chem. Soc.* 33, 496–501 (1901); *Cent.* 1901, II 1201.

3:7240 3-CHLOROPENTENE-2

C_5H_9Cl Beil. I —; I_1—; I_2-(185)

B.P. 91–92° (1); 90–92° at 781 mm. (2) $D_{20}^{20} = 0.9125$ (2) $n_D^{20} = 1.423$ (1)

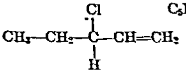
Two geometrical stereoisomers of C̄ are possible but as yet unrecognized.

[For prepn. of C̄ (together with 2-chloropentene-2 (3:7285) and other prods.) from methyl *n*-propyl ketone (1:5415) with PCl_5 see (1); for prepn. of C̄ (together with other prods.) from diethyl ketone (propione) (1:5420) with PCl_5 (1) followed by treatment with alc. KOH (2) see (1) (2).]

C̄ with $NaNH_2$ in xylene at 130° gives (3) a little pentyne-2 (1:8040) and on subsequent pouring of the reactn. mixt. into water also pentyne-1 (1:8025).

3:7240 (1) [illegible] 1925). [illegible] (3) [illegible]

3:7260 3-CHLOROPENTENE-1 C_5H_9Cl Beil. I —
(α-Ethylallyl chloride) I_1—
I_2-(182)



B.P. 93–94° at 759.3 mm. (1) $n_D^{23} = 1.4224$ (4)
92–93° (2) (3)
50–50.2° at 150 mm. (5) $D_4^{20} = 0.8978$ (1) $n_D^{20} = 1.4254$ (1)

Note: C̄ by virtue of facile allylic transposition is readily converted to an equilibrium mixt. with its synionic isomer, 1-chloropentene-2 (3:7470) q.v.; reactns. of C̄ may therefore frequently yield also the corresponding derivatives of the isomer.

[For prepn. of C̄ (or its mixt. with 1-chloropentene-2 (3:7470)) from ethyl-vinyl-carbinol (penten-1-ol-3) with dry HCl (1) (3) (5) (7), with aq. HCl at 0° (6), with PCl_3 at 45° (4) or in cold with pyridine (7) or dimethylaniline (7) (55–59% (7)), with $SOCl_2$ alone (24% yield (7)) or in ether (24% yield (7)), or with dimethylaniline (43% yield (7)) see indic. refs.] [C̄ is separable from the accompanying isomer by careful fractional distillation (5) (7).]

C̄ on long shaking with aq. Na_2CO_3 gives (7) in very poor yield penten-1-ol-3 accompanied by much penten-3-ol-1 and other products. — C̄ with alc. NaOEt gives (4) the corresp. ethyl ether, viz., 3-ethoxypentene-1, b.p. 102°, $D_-^{23} = 0.7768$, $n_D^{23} = 1.3986$, accompanied by the isomeric 1-ethoxypentene-2, b.p. 123°, $D_-^{23} = 0.7930$, $n_D^{23} = 1.4099$ (4).

[For extensive study of behavior of C̄ with KOAc + AcOH, with AgOAc, with *N*-methylaniline, with diethylamine, etc., see (7); for reactn. of C̄ with phenol in pres. of K_2CO_3 + acetone see (5).]

Ⓓ *N*-(Penten-1-yl-3)phthalimide [*N*-(α-ethylallyl)phthalimide]: colorless cryst. from alc., m.p. 78–79° (7). [From C̄ on htg. with K phthalimide in a s.t. at 190–200° for 2½ hrs.; yield is only about half that obtd. from 1-chloropentene-3, the corresp. deriv. of which always accompanies that from C̄ (7).]

3:7260 (1) Baudrenghien, *Bull. soc. chim. Belg.* **32**, 338 (1923). (2) Mumm, Richter, *Ber.* **73**, 858–860 (1940). (3) Mumm, Hornhardt, Diederichsen, *Ber.* **72**, 107 (1939). (4) Prevost, *Compt. rend.* **187**, 1053–1054 (1928). (5) Lauer, Filbert, *J. Am. Chem. Soc.* **58**, 1388 (1936). (6) Prevost, *Bull. soc. chim.* (4) **49**, 264–267 (1931). (7) Meisenheimer, Link, *Ann.* **479**, 254–277 (1930).

3:7265 β-CHLOROETHYL METHYL ETHER C_3H_7OCl Beil. I - 337
(β-Methoxyethyl chloride) I_1-(170)
I_2-(335)

$$\begin{array}{l} CH_2\,O.CH_3 \\ | \\ CH_2Cl \end{array}$$

B.P.			
92–93° (1) (2)		D_4^{20} = 1.0345 (1)	n_D^{20} = 1.41112 (4)
91° (5)		1.0460 (4)	1.411 (1)
90–91° at 735.7 mm. (3)			
90.5° at 747 mm. (7)		D_4^{15} = 1.0407 (4) (1)	
89.4–89.7° at 763.3 mm. (4)			

Colorless liq. with odor like $CHCl_3$; does not fume in air (3). — Sol. in aq. at room temp. to extent of 8% by wt. (7).

[For prepn. from ethylene chlorohydrin (3:5552) + $(CH_3)_2SO_4$ (60% yield (2)) see (2); for prepn. from β-methoxyethanol (1:6405) with PCl_3 + pyridine (65% yield (6)), or $SOCl_2$ + dimethylaniline (7), or diazomethane (5) see (6) (5) (7); for prepn. from ethylene + *N,N*-dichlorobenzenesulfonamide see (1).]

$\bar{C}$ on shaking with aq. does not hydrolyze (dif from α-chloroethers).

3:7265 (1) Sklyarov, *J. Gen Chem.* (*U S.S.R*) **9**, 2121–2125 (1939); *C A* **34**, 4055 (1940). (2) Jones, Powers, *J. Am Chem. Soc.* **46**, 2531–2532 (1924). (3) Fileti, de Gaspari, *Gazz. chim. ital.* **27**, II 293 (1897). (4) Karvonen, *Ann. Acad Sci. Fennicae* **3-A**, No. 7, 1–103 (1912); *Cent.* **1912**, II 1269; *C A.* **14**, 2175 (1920). (5) Meerwein, Hinz, *Ann* **484**, 17 (1930). (6) Palomaa, Kenetti, *Ber.* **64**, 798 (1931). (7) Bennett, Heathcoat, *J. Chem. Soc* **1929**, 270.

3:7270 ISOBUTYRYL CHLORIDE C_4H_7OCl Beil. II - 293
II_1-(128)
II_2-(262)

$$\begin{array}{lll} CH_3\,CH & — & C{=}O \\ \;\;\;\;\;\;| & & | \\ \;\;\;CH_3 & & Cl \end{array}$$

B.P.		F.P.		
92°	(1) (2)	−90° (7)	D_4^{20} = 1.0174 (8)	n_D^{20} = 1.40789 (8)
91.5–92.5° at 748.2 mm.	(8)			1.4080 (3)
91–92°	(3)			1.4070 (5)
90–92°	(30)			
91° at 735 mm.	(4)			
90–91°	(5)			
85–88° at 680 mm.	(6)			

[For prepn. of $\bar{C}$ from isobutyric acid (1:1030) with PCl_5 (81% yield (9)), with PCl_3 (yield: 94% (6), 75% (2)) (8) (4), with PCl_3 + $ZnCl_2$ (82% yield (9)), with $SOCl_2$ (yield: 90% (30), 75% (4) (5), 70% (10), 44% (9)), with benzoyl chloride (82–88% yield (13)), or with $SiCl_4$ in xylene (52% yield (11)) see indic. refs.; for prepn. of $\bar{C}$ from sodium isobutyrate with $POCl_3$ see (1) (12)]

[$\bar{C}$ with isobutyric acid (1:1030) (14) or $\bar{C}$ with pyridine in ether (15) yields isobutyric anhydride (1:1110), b.p. 182.5°.]

[$\bar{C}$ on passing over Ni at 420° dec. (16) into HCl, CO, CO_2, H_2, CH_4 + propylene; $\bar{C}$ + NH_3 over Al_2O_3 at 490–500° yields (17) isobutyronitrile, b.p. 108°.]

[$\bar{C}$ with Et_3N in dry ether or lgr. at room temp. gives (18) 95% yield triethylamine hydrochloride + 57% yield dimethylketene dimer, cf. also (19) (20).]

[$\bar{C}$ with Cl_2 (31) in CCl_4 gives (12) cf. (21) 60–70% α-chloro-isobutyryl chloride (3:5385) + 30–40% β-chloroisobutyryl chloride (3:9101); $\bar{C}$ with SO_2Cl_2 in pres. of dibenzoyl peroxide gives (22) 20% α-chloroisobutyryl chloride (3 5385) + 80% β-chloro-isobutyryl

chloride (3:9101). — Č with Br_2 htd. in s.t. 4 hrs. at 100° gives mainly (10) α-bromoisobutyryl *bromide*, b.p. 163°.]

[Č added to large excess of certain RMgX cpds. is in part reduced and in part undergoes ordinary coupling with formn. of ketones; e.g., Č with *ter*-BuMgCl in ether gives (5) (4) (3) 63% *ter*-butyl-isopropyl-carbinol + 20% isobutyl alc. + 18% 2,2,4-trimethylpentanone-3; Č with *ter*-AmMgCl gives (3) 44% isobutyl isobutyrate.]

[For reactn. of Č with ethyl sodio-acetoacetate see (6); with ethyl acetoacetate + Mg see (23); with ethyl isobutyrate + triphenylmethylsodium giving 55% yield ethyl α,α,γ,γ-tetramethylacetoacetate see (24).]

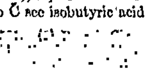
[Č with 2-methylbutene-2 (trimethylethylene) + $SnCl_4$ gives (25) 2-chloro-2,3,5-trimethylhexanone-4, b.p. 74–79° at 14 mm.; Č with cyclohexene + $SnCl_4$ gives (26) 1-cyclohexenyl isopropyl ketone, b.p. 96° at 6 mm.]

[Č with $AlCl_3$ + C_6H_6 gives (27) isobutyrophenone (isopropyl phenyl ketone) (1:5528); Č with $AlCl_3$ + toluene gives (28) isopropyl *p*-tolyl ketone [Beil. VII-331, VII₁-(176)]; Č with $AlCl_3$ + mesitylene gives (29) 75% yield isopropyl mesityl ketone.]

Č on hydrolysis yields isobutyric acid (1:1030), b.p. 154.7°. — For the amide (30), anilide, *p*-toluidide, and other derivs. corresp. to Č see isobutyric acid (1:1030).

3:7270 [illegible] *Bull. soc. chim. Belg.* 30, 216 (1921). (8) Brühl, *Ann.* 203, 20 (1880). (9) Clark, Bell, *Trans. Roy. Soc. Can.* (3) 27, III 97–103 (1933). (10) Smith, Lowcock, *Ber.* 45, 2358–2359 (1912).
(11) Montonna, *J. Am. Chem. Soc.* 49, 2114–2116 (1927). (12) Michael, *Ber.* 34, 4054–4055 (1901). (13) Brown, *J. Am. Chem. Soc.* 60, 1325–1328 (1938). (14) Toennies, Staub, *Ber.* 17, 850–851 (1884). (15) Wedekind, *Ber.* 34, 2073 (1901). (16) Mailhe, *Compt. rend.* 180, 1112 (1925). (17) Mailhe, *Bull. soc. chim.* (4) 23, 380 (1918); *Ann. chim.* (9) 13, 212 (1920). (18) [illegible] 25, 58–60 (1945).
(31) Schmidt, Schloffer (to I.G.) Ger. 738,398, July 15, 1943; *C.A.* 38, 3992 (1944).

3:7275 *d,l*-3-CHLORO-2-METHYLBUTANE $C_5H_{11}Cl$ Beil. I - 135
(*sec.*-Isoamyl chloride; I_1-(40)
isopropyl-methyl-carbinyl chloride) I_2—



B.P. 92.9–93.0° at 760 mm. (1)	D_4^{20} = 0.8685 (4)	n_D^{20} = 1.4081 (4)
91.8–91.9° at 736 mm. (2)	0.878 (2)	1.4095 (2)
91° at 753 mm. (3)		
45.4° at 150 mm. (1)		
25–27° at 60 mm. (4)		

Stable at b.p., at 100° for 24 hrs., to aq. at room temp. (2). — Č is not present in comml. "mixed amyl chlorides" (1).

[For prepn. of Č from 2-methylbutene-3 (1:8200) + HCl in dark at room temp. in s.t. for 7 months (88% yield (2)), or + HCl at 100° (5) (6), or at −80° in presence of $AlCl_3$ (4)

see indicated refs.] [Note that C̄ cannot be prepd. from the corresp. alc., 2-methylbutanol-3 (1:6170) + HCl since only *ter*-amyl chloride (3:7220) results (11).]

[For formn. of C̄ from either 2-methylbutene-1 (1:8210) or 2-methylbutene-2 (1:8220) at −80° in presence of $AlCl_3$ see (7); from isoamyl alcohol (1:6200) + HCl over Al_2O_3 at 430° see (8); from isoamyl chloride (3:7365) over $ThCl_4$ or $BaCl_2$ at 250°, finally over pumice at 200°, see (9); from 2-methylbutane (1:8500) + Cl_2 see (10) (1).]

[For study of reactn. of C̄ with Na see (12) (13).]

C̄ with Mg in dry ether yields (1) (2) corresponding R.Mg.Cl whose treatment with dry O_2 followed by hydrolysis yields (1) (2) 2-methylbutanol-3 (1:6170); [3,5-dinitrobenzoate, cryst. from dil. MeOH (1) or dil. EtOH (2), m.p. 76° (1) (2); *N*-(α-naphthyl)-carbamate, cryst. from pet. eth., m.p. 111–112° (2) (1).] — This R.Mg.Cl should also react according to method of (11) with phenyl isocyanate to yield isopropyl-methyl-acetanilide, m.p. 78 4° (14), 75° (15), although the execution of this reactn. is not recorded.

C̄ with excess $N/10$ $AgNO_3$ is practically completely hydrolyzed in 60 hrs. (2) [dif. from isoamyl chloride (3:7365) which reacts only to extent of 3–4%].

3:7275 (1) Hass, McBee, Weber, *Ind. Eng. Chem.* **27**, 1192–1195 (1935). (2) Whitmore, Johnston, *J. Am. Chem Soc* **55**, 5020–5022 (1933). (3) Wyschnegradsky, *Ann* **190**, 357 (1877). (4) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* **52**, 519 (1933). (5) Berthelot, *Ann.* **127**, 71 (1863). (6) Wurtz, *Ann* **129**, 368 (1864). (7) Leendertse, Tulleners, Waterman, *Rec. trav. chim.* **53**, 717 (1934). (8) Sabatier, Mailhe, *Compt rend.* **169**, 124 (1919). (9) Sabatier, Mailhe, *Compt. rend* **156**, 658 (1913) (10) Aschan, *Cent.* **1918**, II 939.

(11) Underwood, Gale, *J. Am. Chem. Soc.* **56**, 2117 (1934). (12) Morton, LeFevre, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 757 (1936) (13) Morton, Hechenbleikner, *J. Am. Chem. Soc.* **58**, 1699 (1936) (14) Hommelen, *Bull. soc. chim. Belg.* **42**, 249 (1933). (15) Crossley, Perkin, *J. Chem. Soc.* **73**, 17 (1898).

3:7280 2-CHLOROPENTENE-1

$CH_3.CH_2.CH_2.C(Cl){=}CH_2$ C_5H_9Cl Beil. I-210, I_1—, I_2—

B.P. 95–97° (1)

The structure of this material is inadequately supported; the prod. may very possibly be identical with 2-chloropentene-2 (3:7285) q.v.

[For prepn. of C̄ from 2,2-dichloropentane (3:7755) with alc. KOH see (1).]

C̄ on further treatment with alc. KOH yields (1) pentyne-1 (1:8025), b.p. 39.7°.

3:7280 (1) Bruylants, *Ber.* **8**, 411 (1875).

3:7285 2-CHLOROPENTENE-2

$CH_3.CH_2.CH{=}C(Cl).CH_3$ C_5H_9Cl Beil. I—, I_1—, I_2-(185)

B.P. 95–97° (1)
88–89° at 760 mm. (2)
45° at 130 mm. (2)

D_-^{24} = 0.903 (2) **n_D^{24} = 1.421 (2)**

Two geom. stereoisomers of C̄ are possible but as yet unrecognized.

[For prepn. of C̄ from 2,2-dichloropentane (3:7755) with boilg. 10% alc. KOH see (1); from pentanone-2 (1:5415) with PCl_5 see (2).]

C̄ with conc. H_2SO_4 followed by aq. yields (1) methyl-*n*-propyl ketone (pentanone-2 (1:5415), b p. 102°.

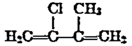
[C̄ with $NaNH_2$ in xylene at 130° followed by ice water gives (3) pentyne-1 (1:8025).]

C̄ on oxidn. with $KMnO_4$ yields (1) propionic acid (1:1025) + AcOH (1:1010).

3:7285 (1) Lemke, Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **7**, 1995–1998 (1937); *Cent.* **1939**, I 2398; *C.A.* **32**, 482 (1938). (2) Bourgeul, *Ann. chim.* (10) **3**, 369–370 (1925); *Bull. soc. chim.* (4) **35**, 1633 (1924). (3) Bourgeul, *Ann. chim.* (10) **3**, 220, 370 (1925).

3:7290 3-CHLORO-2-METHYLBUTADIENE-1,3 C_5H_7Cl Beil. S.N. 12

(2-Chloro-3-methylbutadiene-1,3;
"β-Chloroisoprene")



B.P. 93° at 760 mm. (1) $D_4^{20} = 0.9593$ (1) $n_D^{20} = 1.4689$ (1)
41° at 113 mm. (1) (2)
37° at 105 mm. (1)

[For prepn. of C̄ (40% yield (1)) from 2-methylbutene-1-yne-3 by treatment as specified (1) with HCl + Cu_2Cl_2 + NH_4Cl see (1) (2) (10); for prepn. (60% yield (3) (4)) from 2,3,3-trichloro-2-methylbutane (3:4755) with quinoline (2 moles) at 140–225° see (3) (4).]

C̄ readily polymerizes; for details see (1) (2). [For prepn. of plastic polymers from C̄ see (5).]

C̄ htd. in s.t. 16 hrs. at 160° with SO_2 in ord. (not dry) ether yields (6) (7) (10) by 1,4-addition a compd. designated (6) (7) as 1,1-dioxo-3-chloro-4-methylthiacyclopentene-3, ndls. from aq. (7) or alc. (6), m.p. 120.0–120.5° (6) (7). [For extensive study of this prod. see (7).] [The corresponding selenium analog, in very poor (2%) yield from C̄ + SeO_2 in $CHCl_3$ (8), has m.p. 110° dec. (8).]

C̄ (1 g.) with 1,4-naphthoquinone (1:9040) htd. at 100° for ½ hr. gives (1) on cooling 2-chloro-3-methyltetrahydroanthraquinone, white ndls. from acetone, m.p. 165–166° u.c. (1); this prod. on suspension in dil. alc. NaOH and oxidn. of the blue soln. with air until yel., followed by dilution with aq., gives (1) 2-chloro-3-methylanthraquinone, cryst. from AcOH, m.p. 214–215° u.c. (1), 215° u.c. (9).

3:7290 (1) Carothers, Coffman, *J. Am. Chem. Soc.* **54**, 4071–4076 (1932). (2) Carothers, Coffman (to du Pont), U.S. 1,950,441, March 13, 1934; Ger. 588,708, Nov. 24, 1933; Brit. 395,301, Oct. 10, 1933; *Cent.* **1934**, II 1038. (3) Tishchenko, *J. Gen. Chem.* (*U.S.S.R.*) **6**, 1116–1132 (1936); *Cent.* **1937**, I 573; *C.A.* **31**, 1003 (1937). (4) Tishchenko, Russ. 44,249, Sept. 20, 1935; *Cent.* **1936**, I 3575; *C.A.* **32**, 2962 (1938). (5) du Pont Co., Brit. 529,838, Nov. 29, 1940; *C.A.* **35**, 7758 (1941); French 853,478, Mar. 20, 1940; *C.A.* **36**, 2650 (1942). (6) Backer, Strating, *Rec. trav. chim.* **53**, 542–543 (1934). (7) Backer, van der Baan, *Rec. trav. chim.* **56**, 181–185 (1937). (8) Backer, Strating, *Rec. trav. chim.* **53**, 1118 (1934). (9) Keimatsu, Hirano, *J. Pharm. Soc. Japan* **49**, 140–147 (1929); *C.A.* **23**, 3466 (129). (10) Backer, Blass, *Rec. trav. chim.* **61**, 785–801, 924 (1942); *Cent.* **1943**, I 1567–1569; *C.A.* **38**, 3646–3647 (1944).

3:7295 ETHYL CHLOROFORMATE ClCO.OC$_2$H$_5$ $C_3H_5O_2Cl$ Beil. III - 10 III$_1$-(5) III$_2$-(10)

("Ethyl chlorocarbonate")

B.P.			F.P.	
[95°	at 760 mm.	(1)]	−80.6° (1)	$D_4^{25} = 1.127$ (10)
[94–95° cor.		(2)]		$n_D^{21.2} = 1.3949$ (8)
94°	at 773 mm.	(3)		
93.1°	at 760 mm.	(4)		$D_4^{20} = 1.13519$ (4)
93.0°	at 760 mm.	(5)		1.1377 (6)
92.6–93.0°	at 768 mm.	(6)		$n_D^{20} = 1.39738$ (4)
92.5–93.5°		(7)		$D_4^{15} = 1.14419$ (4)
91.3–91.35°	at 729.6 mm.	(8)		1.1418 (9)
91.5°		(10)		See Note 1.

Note 1. For D_4^t between −75.5° (1.278) and +84.8° (1.022) see (10).